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Physics. — *"On the Course of the Values of a and b for Hydrogen at Different Temperatures and Volumes"*. III. By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of Febr. 23, 1918).

Continuation of § XVI.

The factor by which the double integrals (7) are multiplied, now becomes, with $n = N : v$:

$$\tfrac{1}{3}\pi n a^2 \times MN = \tfrac{1}{2} \times \tfrac{2}{3}\pi N s^3 \times MN \times \frac{a^2}{s^3} \times \frac{1}{v},$$

i. e., as $\tfrac{2}{3}\pi N s^3 = 4m = (b_g)_\infty$, $MN = \alpha$:

$$\tfrac{1}{2} \times (b_g)_\infty \times \alpha \times \frac{a^2}{s^3} \times \frac{1}{v} = \omega \times \frac{a^2}{s^3} \times \frac{1}{v}.$$

With omission of $1 : v$ we get, therefore, for the constant of attraction a:

$$\mathrm{a} = \omega \times \frac{2a^4}{s(a^2-s^2)}\left[\int_{\theta_0}^{90}\int_{r_m}^{a} \frac{dr \times \sin\theta d\theta}{r^2\sqrt{1-\frac{a^2}{r^2}\sin^2\theta + \varphi\left(\frac{a^2}{r^2}-1\right):\left(\frac{a^2}{s^2}-1\right)}} + \int_{0}^{\theta_0}\int_{s}^{a} ibid.\right],$$

when also for $F(r)$ and $-F'(r)$ their values according to (8) and (8a) are substituted. When to abbreviate we write k^2 for $s^2 : (a^2 - s^2)$, the above becomes:

$$\mathrm{a} = \omega \times \frac{2a^4}{s(a^2-s^2)}\left[\int_{\theta_0}^{90}\int_{r_m}^{a} \frac{dr \times \sin\theta d\theta}{r\sqrt{r^2 - a^2\sin^2\theta + k^2\varphi(a^2-r^2)}} + \int_{0}^{\theta_0}\int_{s}^{a} ibid.\right], \ldots (7^a)$$

in which, therefore, $\omega = \tfrac{1}{2} \times (b_g)_\infty \times \alpha$.

Let us first discuss the first integral referring to all the molecules that pass the molecule which is supposed not to move, without coming in collision with it. We may write for it:

$$I_1 = \int_{\theta_0}^{90}\int_{r_m}^{a} \frac{dr \times \sin\theta d\theta}{r\sqrt{a^2\cos^2\theta - (a^2-r^2)(1-k^2\varphi)}}.$$

As was already remarked above, the above calculations only hold for temperatures *above* a certain limiting temperature T_0, defined

by $\theta_0 = 90°$, $\sin\theta_0 = 1$. This is namely the lowest temperature at which a value for θ_0 is still possible. From (6) follows namely $\sin^2\theta_0 = \frac{s^2}{a^2}(1+\varphi)$, so that $\frac{s^2}{a^2}(1+\varphi)$ can never become greater than 1, hence φ never greater than $(a^2-s^2):s^2 = 1:k^2$.

When we represent this limiting value of $\varphi = M:\frac{1}{2}\mu u_0^2$ by φ_0, we get therefore

$$\varphi_0 = \frac{1}{k^2} = \frac{1-n^2}{n^2}, \quad \ldots\ldots\ldots \quad (9)$$

when we put the ratio $s:a = n$. Accordingly, as long as φ remains $< \varphi_0$ $(T > T_0)$, the quantity $1-k^2\varphi$ also remains > 0 in the above integral.

θ_0 is $= 90°$ in the limiting case $\varphi = \varphi_0$; then *all* the entering molecules collide, also those that strike at an angle $\theta = 90°$, which just reach the rim of the sphere $r = s$, and will yield there a minimum value for r for the last time.

But as soon as the temperature becomes still lower, and φ becomes $> \varphi_0$, all the entering molecules collide without previous minimum, i. e. they all strike at angles $< 90°$ with the normal. For *these* values of φ we shall therefore have to execute a *separate* integration later on, i. e. for all the values from $\varphi > \varphi_0$ to $\varphi = \infty$ $(T = 0)$.

Now the integration with respect to r yields:

$$\int_{r_m}^{a} \frac{dr}{r\sqrt{p^2r^2-a^2(p^2-\cos^2\theta)}} = \frac{1}{a\sqrt{p^2-\cos^2\theta}}\left(Bg\,tg\sqrt{\frac{p^2r^2-a^2(p^2-\cos^2\theta)}{a^2(p^2-\cos^2\theta)}}\right)_{r_m}^{a},$$

when we put $1-k^2\varphi = p^2$. As $\sin^2\theta_0 = \frac{s^2}{a^2}(1+\varphi)$, $\cos^2\theta_0$ is therefore $= 1-\frac{s^2}{a^2}(1+\varphi) = \frac{a^2-s^2}{a^2}\left(1-\frac{s^2}{a^2-s^2}\varphi\right) = \frac{a^2-s^2}{a^2}p^2$. Hence the quantity p^2 is also $= \frac{a^2}{a^2-s^2}\cos^2\theta_0$, so that $p^2-\cos^2\theta$ always remains positive. For $\cos^2\theta$ is at most $= \cos^2\theta_0$ in I_1.

At the limit r_m the quantity under the rootsign, viz. $p^2r^2-a^2(p^2-\cos^2\theta)$ is always $= 0$, because then $dr:dt = 0$ (compare (3^a)). Hence we have after introduction of the limits:

$$I_1 = \frac{1}{a}\int_{\theta_0}^{90} \frac{\sin\theta\,d\theta}{\sqrt{p^2-\cos^2\theta}}\,Bg\,tg\frac{\cos\theta}{\sqrt{p^2-\cos^2\theta}} = \frac{1}{a}\int_{0}^{x_0}\frac{dx}{\sqrt{p^2-x^2}}\,Bg\,tg\frac{x}{\sqrt{p^2-x^2}},$$

when we write $-d\cos\theta$ for $\sin\theta d\theta$, and x for $\cos\theta$, so that $\cos\theta_0$ is represented by x_0. Now $dBgtg = dx:\sqrt{p^2-x^2}$, so that we find:

$$I_1 = \frac{1}{2a} Bg^2\, tg \frac{x_0}{\sqrt{p^2 - x_0^2}} = \frac{1}{2a} Bg^2\, tg \frac{1}{k},$$

as $p^2 = \frac{a^2}{a^2 - s^2} x_0^2$ (see above), hence $p^2 - x_0^2 = \frac{s^2}{a^2 - s^2} x_0^2 = k^2 x_0^2$.

Multiplying by the factor $\omega \times \frac{2a^4}{s(a^2 - s^2)}$, we have therefore for the first part of a:

$$a_1 = \omega \times \frac{a^3}{s(a^2 - s^2)} Bg^2\, tg \frac{1}{k} = \omega \times \frac{1}{n(1 - n^2)} Bg^2\, tg \frac{\sqrt{1 - n^2}}{n} \quad . \quad (10)$$

Hence we find for this a value which no longer contains φ (hence T), so that the part of the constant of attraction which refers to the *passing* molecules, appears to be *independent of the temperature*. This seems somewhat strange, because near the limiting temperature, given by φ_0, θ_0 gets near 90°, so that then the limits of I_1 with respect to θ get nearer and nearer to each other, and finally coincide at $\theta_0 = 90°$ ($\varphi = \varphi_0$). It would therefore be expected that a_1 would become smaller and smaller according as T decreases, and that it would disappear at the limiting temperature. However, this is not the case according to (10). The explanation may be found by an examination of the paths of the molecules, which shows that with the diminution of the velocity u_0 they occupy an *ever larger portion of the path* within the sphere of attraction; to which the circumstance is added that the frequency for the angle, which is proportional to $\sin\theta$, reaches its *maximum* exactly in the neighbourhood of $\theta = 90°$.

When n is *near* 1, i. e. a near s (very thin sphere of attraction), $Bg^2 tg$ approaches $\frac{1 - n^2}{n^2}$, so that then a_1 approaches $\underline{\omega : n^3 = \omega}$. As $\sin^2\theta_0$ is $= \frac{s^2}{a^2}(1 + \varphi)$, $\cos^2\theta_0 = x_0^2 = 1 - \frac{s^2}{a^2}(1 + \varphi)$, so that x_0^2 will lie between $\frac{a^2 - s^2}{a^2} = 1 - n^2 = \pm 0$ at high temperatures ($\varphi = 0$), and (0) at lower temperatures ($\varphi = \varphi_0$). θ_0 lies, therefore, in both cases in the neighbourhood of 90°, hence the limits of integration of I_1 will almost coincide, viz. θ between $\pm$ 90° and 90° at high temperatures, resp. (90°) and 90° at lower temperatures.

In the case $n = 1$ the limiting value $\varphi_0 = (1 - n^2) : n^2$ will lie near 0, i.e. T_0 *near* ∞, so that the available range of temperature is exceedingly small.

If, however, n is *near* 0, i.e. a very much larger than s (very

large sphere of attraction), then Bg^2tg approaches [1]) $^1/_4\pi^2 - \pi n$, hence a_1 approaches $\omega \times \frac{1}{n} \times \frac{1}{4}\pi^2 = \infty$. Now x_0^2 lies between $1-n^2 = \pm 1$ at high temperatures and (0) at low temperatures, so that at high temperatures θ will lie between $\pm$ 0° and 90°, and at low temperatures between (90°) and 90°. And the limiting value of φ_0 is near ∞, i.e. T_0 near 0, so that the available range of temperature is very large in this case. That a_1 now becomes *infinite*, is not astonishing, for to obtain a *finite* value, $F(r)$ should decrease much more rapidly with r than is the case on our assumption (8) — viz. in inverse ratio to r^3. This assumption, however, only holds for not too large values of $a : s$.

§ XVII. Calculation of $(a_2)_1$.

Now we must carry out the second integration in (7[a]). This applies, therefore, to all the molecules that can come in *collision*, as θ now remains smaller than the limiting angle θ_0. It should be carried out in *two* stages, viz. from $x\ (= cos\,\theta) = p$ to $x = x_0$, and from $x = 1\ (\theta = 0)$ to $x = p$. For in the general integral with respect to r (see § XVI), viz.

$$\int_s^a \frac{dr}{r\sqrt{p^2 r^2 - a^2 (p^2 - cos^2\,\theta)}},$$

$p^2 - cos^2\,\theta = p^2 - x^2$ will be *positive* in the first case, *negative* on the other hand in the second case. Accordingly the first stage gives rise to a *Bgtg*, the second to a *log*. The first stage, integrated with respect to r, yields:

$$\frac{1}{a\sqrt{p^2-x^2}}\left(Bg\,tg\sqrt{\frac{p^2 r^2 - a^2(p^2-x^2)}{a^2(p^2-x^2)}}\right)_s^a =$$

$$= \frac{1}{a\sqrt{p^2-x^2}}\left[Bg\,tg\,\frac{x}{\sqrt{p^2-x^2}} - Bg\,tg\,\frac{\sqrt{x^2-x_0^2}}{\sqrt{p^2-x^2}}\right],$$

because $p^2\left(1 - \frac{s^2}{a^2}\right)$ is $= x_0^2$ (see § XVI). Hence we have:

$$(I_2)_1 = \frac{1}{a}\left[\int_{x_0}^{p} \frac{dx}{\sqrt{p^2-x^2}}\,Bg\,tg\,\frac{x}{\sqrt{p^2-x^2}} - \int_{x_0}^{p} \frac{dx}{\sqrt{p^2-x^2}}\,Bg\,tg\,\frac{\sqrt{x^2-x_0^2}}{\sqrt{p^2-x^2}}\right].$$

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[1]) $Bgtg\,\frac{\sqrt{1-n^2}}{n}$ is namely $= Bgtg\,\frac{1}{n} = Bg\,cos\,n = \frac{1}{2}\pi - n$, hence $Bg^2tg = \frac{1}{4}\pi^2 - \pi n$.

The first integral yields $\frac{1}{2}\left(Bg^2tg\,\frac{x}{\sqrt{p^2-x^2}}\right)_{x_0}^{p}=\frac{1}{2}\left[\frac{1}{4}\pi^2-Bg^2tg\,\frac{1}{k}\right]$,

as $d\,Bgtg$ is again $=\frac{dx}{\sqrt{p^2-x^2}}$.

But the second integral cannot so easily be integrated. As then $d\,Bgtg$ is $=\frac{x}{\sqrt{x^2-x_0^2}}\,\frac{dx}{\sqrt{p^2-x^2}}$, the said integral becomes:

$$\int_{x_0}^{p}\frac{\sqrt{x^2-x_0^2}}{x}\,Bg\,tg\times d\,Bg\,tg=\int_{0}^{\infty}\frac{y\sqrt{p^2-x_0^2}}{\sqrt{p^2y^2+x_0^2}}\,Bg\,tg\,y\times d\,Bg\,tg\,y,$$

when we put $(x^2-x_0^2):(p^2-x^2)=y^2$, which causes x^2 to become $(p^2y^2+x_0^2):(1+y^2)$, and $x^2-x_0^2$ to become $y^2(p^2-x_0^2):(1+y^2)$. With $Bgtgy=\psi$ the last integral passes into:

$$\frac{\sqrt{p^2-x_0^2}}{p}\int_0^{1/2\pi}\frac{tg\,\psi}{\sqrt{tg^2\,\psi+(x_0^2:p^2)}}\,\psi\,d\psi=\frac{s}{a}\int_0^{1/2\pi}\frac{sin\,\psi}{\sqrt{sin^2\psi+\frac{a^2-s^2}{a^2}\,cos^2\psi}}=$$

$$=k\int_0^{1/2\pi}\frac{sin\,\psi}{\sqrt{1+k^2\,sin^2\,\psi}}\,\psi\,d\psi,$$

as $\sqrt{p^2-x_0^2}:p$ in consequence of $p^2=\frac{a^2}{a^2-s^2}\,x_0^2$, hence $p^2-x_0^2=$

$=\frac{s^2}{a^2-s^2}\,x_0^2$, can be replaced by $\frac{s}{a}$, and $x_0^2:p^2$ by $(a^2-s^2):a^2$, while further

$$sin^2\,\psi+\frac{a^2-s^2}{a^2}\,cos^2\,\psi=\frac{a^2-s^2}{a^2}+\frac{s^2}{a^2}\,sin^2\,\psi=\frac{a^2-s^2}{a^2}\left(1+\frac{s^2}{a^2-s^2}\,sin^2\,\psi\right)$$

and $s^2:(a^2-s^2)=k^2$. The last transcendental, quasi-elliptical integral can now easily (see appendix) be developed into a series, and then be approximated. Previously we may observe that x_0, hence φ (and therefore also T), no longer occur in it, so that the result — like that of the first part of $(I_2)_1$ — *will not be dependent on the temperature*, as little as this was the case with I_1 (see § XVI). It is further easy to see that the said integral approaches

$$\int_0^{1/2\pi}\frac{k\,sin\,\psi}{\sqrt{k^2\,sin^2\,\psi}}\,\psi d\psi=(\tfrac{1}{2}\,\psi^2)_0^{1/2\pi}=\tfrac{1}{2}\times\tfrac{1}{4}\,\pi^2$$ in the limiting case $n=1$

($a = s$), hence $k = \infty$; and in the opposite limiting case $n = s$ ($a : s = \infty$), hence $k = 0$, approaches $k \int_0^{1/2\pi} sin\ \psi \times \psi\ d\psi = k\Big(-\psi\ cos\ \psi + \int cos\ \psi\ d\psi\Big) = k\ (-\psi\ cos\ \psi + sin\ \psi)$, which yields the value k between 0 and $^1/_2\pi$.

Hence the integral in question lies between $^1/_8\pi^2$ and $k = s : \sqrt{a^2 - s^2} = s : a = n$ (as in the latter case s is infinitely small with respect to a), so that we can represent it by

$$\varepsilon n \times {}^1/_8\pi^2,$$

in which ε will lie between $\underline{1}$ (when $n = 1$) and $8 : \pi^2 = \underline{0{,}811}$ (when $n = 0$). Accordingly the factor ε is little variable. It appears from the expansion into series (see Appendix *A*), that ε becomes $= 0{,}845$ for $n = 0{,}6$ (i. e. $s = 0{,}6a$).

We now have:

$$(I_2)_1 = \frac{1}{2a}\left[\left(\tfrac{1}{4}\pi^2 - Bg^2\ tg\ \frac{1}{k}\right) - \varepsilon n \times \tfrac{1}{4}\pi^2\right],$$

so that taking the factor $\omega \times (2a^4 : s(a^2 - s^2))$ into account, the following equation is found:

$$(a_2)_1 = \omega \times \frac{1}{n(1-n^2)}\left[\tfrac{1}{4}\pi^2(1 - \varepsilon n) - Bg^2\ tg\ \frac{\sqrt{1-n^2}}{n}\right] \quad . \quad (11)$$

If *n is near* 1 (a ~ s), this approaches $\omega \times \frac{1}{1-n^2}[\frac{1}{4}\pi^2(1-n) - (1-n^2)] = \underline{= \omega \times (\frac{1}{8}\pi^2 - 1) = 0{,}234\ \omega}$. The limits of integration p and x_0 are determined by $x_0^2 = 1 - \frac{s^2}{a^2}(1+\varphi) = \frac{a^2 - s^2}{a^2} = 1 - n^2 = \pm 0$ at high temperatures ($\varphi = 0$), resp. (0) at lower temperatures ($\varphi = \varphi_0$), and $p^2 = \frac{a^2}{a^2 - s^2}\ x_0^2 = (1)$, resp. (0); so that θ lies between (0°) and ± 90° at high temperatures, and (90°) and (90°) at lower temperatures.

And if n *is near* 0 (a great with respect to s), then $(a_2)_1$ approaches to $\omega \times \frac{1}{n} \times [(\frac{1}{4}\pi^2 - 2n) - (\frac{1}{4}\pi^2 - \pi n)] = \underline{\omega \times (\pi - 2) = 1{,}14\ \omega}$. Then we have as limits of integration ± 1 for x_0 ($\varphi = 0$), resp. (0) at $\varphi = \varphi_0$, and (1), resp. (0) for p; so that θ lies between (0°) and ± 0° at high temperatures, and (90°) and (90°) at low temperatures.

When $(a_2)_1$ is added to a_1, we find for the part of the constant of attraction a that is *independent of the temperature* (coming from

the passing molecules and from the (not central) colliding molecules):

$$a_\infty = a_1 + (a_2)_1 = \omega \times \frac{1-\varepsilon n}{n(1-n^2)} \tfrac{1}{4}\pi^2 \quad . \quad . \quad . \quad . \quad (12)$$

According to the above this part comprises the *almost totality* of the angles of incidence, from 90° to near to 0°, at *high* temperatures; and only a *very small part*, from 90° to near to 90° at *low* temperatures; i. e. in the limiting cases $n \to 1$ and $n \to 0$. But also in intermediate cases this continues to hold, because at high temperatures p^2 always lies in the neigbourhood of $\frac{a^2}{a^2-s^2} \times \frac{a^2-s^2}{a^2} = 1$, and at low temperatures always in the neighbourhood of $\frac{a^2}{a^2-s^2} \times 0 = 0$.

Hence the region left for the part of a that is *dependent on* the temperature, is the greater as the temperature becomes smaller.

Now the quantity a_∞ in (12) lies between $\omega \times \frac{1-n}{n(1-n^2)} \tfrac{1}{4}\pi^2 = \omega \times \frac{1}{n(1+n)} \tfrac{1}{4}\pi^2 = \omega \times \tfrac{1}{8}\pi^2$ for $n = 1$, and $\omega \times \frac{1}{n} \times \tfrac{1}{4}\pi^2 = \infty$ for $n = 0$.

§ XVIII. Calculation of $(a_2)_2$.

We finally come to the calculation of the part that is dependent on the temperature, and corresponds with the more central collisions of the *second* stage of I_2. We now have for the integration with respect to r (cf § XVII):

$$\int_s^a \frac{dr}{r\sqrt{p^2r^2 + a^2(\cos^2\theta - p^2)}},$$

in which $\cos^2\theta - p^2$ remains *positive* between the limits $\theta = 0°$ and $\theta = Bg \cos p$. The integral yields:

$$\frac{1}{a\sqrt{x^2-p^2}} \left(\log \frac{\sqrt{p^2r^2 + a^2(x^2-p^2)} - a\sqrt{x^2-p^2}}{r} \right)_s^a =$$

$$= \frac{1}{a\sqrt{x^2-p^2}} \left[\log (x - \sqrt{x^2-p^2}) - \log \frac{a}{s}(\sqrt{x^2-x_0^2} - \sqrt{x^2-p^2}) \right],$$

when $\cos\theta$ is put again $= x$, and $\cos\theta_0 = x_0$, x_0^2 being $= p^2\left(1-\frac{s^2}{a^2}\right)$ (Cf. § XVI). Hence we have:

$$(I_3)_7 = \frac{1}{a}\left[\int_p^1 \frac{dx}{\sqrt{x^2-p^2}} \log \frac{x-\sqrt{x^2-p^2}}{p} - \int_p^1 \frac{dx}{\sqrt{x^2-p^2}} \log \frac{\sqrt{x^2-x_0^2}-\sqrt{x^2-p^2}}{s/a\, p}\right].$$

We have written $-dx$ for $\sin\theta d\theta = -d\cos\theta$. The minus sign has again been removed by reversing the limits of integration. Besides — for the sake of homogeneity — a factor p has still been introduced under both *log*. For $s/a\, p$ we may also write $\sqrt{p^2-x_0^2}$.

The first integral can again be easily integrated. $d\,log$ is namely $= -\frac{dx}{\sqrt{x^2-p^2}}$, so that we find for it:

$$\tfrac{1}{2} log^2 \left(\frac{x-\sqrt{x^2-p^2}}{p}\right)_1^p = -\tfrac{1}{2} log^2 \frac{1-\sqrt{1-p^2}}{p} = -\tfrac{1}{2} log^2 \frac{p}{1+\sqrt{1-p^2}},$$

for which with a view to log^2 also $-\tfrac{1}{2} log^2 \frac{1+\sqrt{1-p^2}}{p}$ may be written.

The second presents again the same difficulties as the corresponding *Bgtg* in § XVII. This becomes namely, $d\,log$ now being $=$

$$= -\frac{x}{\sqrt{x^2-x_0^2}} \frac{dx}{\sqrt{x^2-p^2}}:$$

$$-\int_p^1 \frac{\sqrt{x^2-x_0^2}}{x} log \times d\,log = \int_1^p \frac{\sqrt{p^2-x_0^2}}{\sqrt{p^2-y^2x_0^2}} log \sqrt{\frac{1-y}{1+y}} \times d\,log,$$

seeing that

$$log \frac{\sqrt{x^2-x_0^2}-\sqrt{x^2-p^2}}{\sqrt{p^2-x_0^2}} = log \sqrt{\left(1-\sqrt{\frac{x^2-p^2}{x^2-x_0^2}}\right):\left(1+\sqrt{\frac{x^2-p^2}{x^2-x_0^2}}\right)},$$

while from $(x^2-p^2):(x^2-x_0^2) = y^2$ follows $x^2 = (p^2-y^2x_0^2):(1-y^2)$ and $x^2-x_0^2 = (p^2-x_0^2):(1-y^2)$. Now $log \sqrt{\frac{1-y}{1+y}} = -Bgtg\, hyp\, y$, so that we find with $Bg\,tg\,h\,y = \psi$:

$$\frac{\sqrt{p^2-x_0^2}}{p} \int_1^p \frac{1}{\sqrt{1-\frac{x_0^2}{p^2}\, tg^2h\,\psi}}\, \psi\, d\psi = k \int_{tg\,\theta_0:k}^1 \frac{\cos h\,\psi}{\sqrt{1+k^2\cos^2h\,\psi}}\, \psi\, d\psi,$$

because $\frac{a^2-s^2}{a^2} + \frac{s^2}{a^2}\cos^2h\,\psi$ can be substituted for $\cos^2h\,\psi - \frac{a^2-s^2}{a^2} \times$ $\times \sin^2h\,\psi$, with $\sin^2h\,\psi = \cos^2h\,\psi - 1$; and $s^2:(a^2-s^2)$ is $= k^2$ (see § XVII). For $x_0^2:p^2$ we may namely write $(a^2-s^2):a^2$, and $(p^2-x_0^2):p^2$

is $= s^2 : a^2$. The limits for x are 1 and p, hence $\sqrt{\frac{1-p^2}{1-x_0^2}}$ and 0 for y, i. e. for $tg\,h\,\psi$. Thus $\sqrt{\frac{1-x_0^2}{p^2-x_0^2}}$ and 1 for $cos\,h\,\psi = 1 : \sqrt{(1-tg^2 h\,\psi)}$, or $tg\,\theta_0 : k$ and 1; $p^2-x_0^2$ being $= k^2 x_0^2$, and x_0^2 being $cos^2\,\theta_0$. Evidently the limits for ψ are $log \frac{\sqrt{1-x_0^2}+\sqrt{1-p^2}}{\sqrt{p^2-x_0^2}} =$

$$= log\left(\frac{tg\,\theta_0}{k} + \sqrt{\frac{tg^2\,\theta_0}{k^2} - 1}\right) \text{and } 0,$$

as

$$Bg\,tg\,h\,\psi = - log \frac{\sqrt{x^2-x_0^2}-\sqrt{x^2-p^2}}{\sqrt{p^2-x_0^2}} = log \frac{\sqrt{x^2-x_0^2}+\sqrt{x^2-p^2}}{\sqrt{p^2-x_0^2}}.$$

In this $tg\,\theta_0 : k$ is > 1, because now $p < 1$.

Thus we obtain an integral of quite the same form as that of § XVII; with only this difference, that now hyperbolical cosinus is put instead of the former sinus. When again we expand into a series (see Appendix B), it appears that both at *high* temperatures ($\varphi = 0$) and at *low* temperature ($\varphi = \varphi_0 = 1 : k^2$) all the terms with higher powers of *log* with respect to the first term disappear, so that with close approximation we may write:

$$-\tfrac{1}{2}\, n \sqrt{1+\varphi}\, log^2 \frac{\sqrt{1+\varphi}+\sqrt{(1+k^2)\,\varphi}}{\sqrt{1-k^2\,\varphi}},$$

in which φ is determined by the relation $\frac{a^2}{s^2}\, sin^2\,\theta_0 = 1 + \varphi$ (cf. equation (6) of the previous paper), in consequence of which $tg^2\,\theta_0 : k^2$ becomes $= (1+\varphi) : (1-k^2\,\varphi)$. ($n$ has again been written for $s : a = k : \sqrt{1+k^2}$).

When we now add the found integral to the first, viz. $\frac{1}{2}\, log^2 \frac{1+\sqrt{1-p^2}}{p}$ then (p^2 being $= \frac{a^2}{a^2-s^2}\, x_0^2 = (1+k^2) x_0^2$, and x_0^2 being $= 1 - sin^2\theta_0$ $= 1 - \frac{k^2}{1+k^2}(1+\varphi)$, so that p^2 becomes $= 1-k^2\,\varphi$) we get:

$$(I_2)_2 = \frac{1}{2a}\left[- log^2 \frac{1+k\sqrt{\varphi}}{\sqrt{1-k^2\,\varphi}} + n\sqrt{1+\varphi}\, log^2 \frac{\sqrt{1+\varphi}+\sqrt{(1+k^2)\,\varphi}}{\sqrt{1-k^2\,\varphi}}\right],$$

so that taking into account the factor $\omega \times (2\,a^4 : s(a^2-s^2))$, we get the following form:

$$(a_2)_2 = \omega \times \frac{1}{n(1-n)^2}\left[n\sqrt{1+\varphi}\ log^2 \frac{\sqrt{1+\varphi}+\sqrt{(1+k^2)\varphi}}{\sqrt{1-k^2\varphi}} - \right.$$

$$\left. - log^2 \frac{1+k\sqrt{\varphi}}{\sqrt{1-k^2\varphi}}\right] \ldots (13)$$

As $log \dfrac{\sqrt{1+\varphi}+\sqrt{(1+k^2)\varphi}}{\sqrt{1-k^2\varphi}} =$

$$= \tfrac{1}{2}\, log \frac{1+\sqrt{\dfrac{(1+k^2)\varphi}{1+\varphi}}}{1-\sqrt{\dfrac{(1+k^2)\varphi}{1+\varphi}}} = \sqrt{\frac{(1+k^2)\varphi}{1+\varphi}} + \tfrac{1}{3}(\ )^3 + \text{etc.}$$

$$log \frac{1+k\sqrt{\varphi}}{\sqrt{1-k^2\varphi}} = \tfrac{1}{2}\, log \frac{1+k\sqrt{\varphi}}{1-k\sqrt{\varphi}} = k\sqrt{\varphi} + \tfrac{1}{3}(\ )^3 + \text{etc.},$$

$(a_2)_2$ will evidently at *high* temperature (φ near 0) approach to

$$(a_2)_2 = \omega \times \frac{1}{n(1-n^2)}\left[n\sqrt{1+\varphi}\ \frac{(1+k^2)\varphi}{1+\varphi} - k^2\varphi\right],$$

i. e. with $k^2 = n^2 : (1-n^2)$ to

$$(a_2)_2 = \omega \times \frac{1}{n(1-n^2)}\left[\frac{n}{1-n^2}\frac{\varphi}{\sqrt{1+\varphi}} - \frac{n^2}{1-n^2}\varphi\right],$$

or $$(a_2)_2 = \omega \times \frac{1}{n(1-n^2)} \times \frac{n}{1+n}\varphi \quad \underline{(\varphi = 0)} \quad , \ldots . \quad (13a)$$

when φ is simply written for $\varphi : \sqrt{1+\varphi}$. This becomes therefore properly $= 0$ for $T = \infty$. Then the limits of the original integral $(I_2)_2$, viz. p and 1, are equal, viz. $= 1$, which causes the limits of the angle of incidence θ to lie between (0°) and 0° (see also the end of § XVII).

For *low* temperatures (φ near $\varphi_0 = 1 : k^2$) we shall have:

$$(a_2)_2 = \omega \times \frac{1}{n(1-n^2)}\left[log^2\left(\frac{1}{n}\frac{2}{\sqrt{1-k^2\varphi}}\right) - log^2 \frac{2}{\sqrt{1-k^2\varphi}}\right],$$

because then $n\sqrt{1+\varphi}$ is $= 1$, and $\sqrt{(1+k^2)\varphi} = \sqrt{1+\varphi} = 1 : n$. And as $log\left(\frac{1}{n}\frac{2}{\sqrt{}}\right) = log\frac{1}{n} + log\frac{2}{\sqrt{}}$, we may finally write with omission of $log^2 \frac{1}{n}$ in comparison with the infinitely large terms:

$$(a_2)_2 = \omega \times \frac{1}{n(1-n^2)} \times log\frac{1}{n^2} \times log \frac{2}{\sqrt{1-k^2\varphi}} \quad \underline{(\varphi = \varphi_0 = 1 : k^2)} \quad . \quad (13b)$$

This gets near to *logarithmically infinite*. Now the limits p and 1 are evidently $= 0$ and 1, so that θ lies between (90°) and 0°, hence comprises the whole region.

When $n \backsim 1$ ($a \backsim s$), $(a_2)_2$ does not become $= \infty$ in 13^a. For as φ can never become greater than $1 : k^2 = (1-n^2) : n^2$, $(a_2)_2$ remains evidently smaller than $\omega \times \frac{1}{n^2(1+n)}$, i.e. $< \omega \times \frac{1}{2}$. Then ($n = 1-\delta$) *log* $(1 : n^2)$ becomes $2\,(1-n)$ in (13^b), so that $(a_2)_2$ will approach $\omega \times log \frac{2}{\sqrt{1-k^2\varphi}}$.

If on the other hand $n \backsim 0$ (a large with respect to s), then $(a_2)_2$ approaches $\omega \times \varphi$ in (13^a), whereas this quantity will approach infinite $\times$ (*log*-infinite)^2 in (13^b), i.e. will greatly increase, when the temperature becomes lower.

§ XIX. Calculation of a.

When we finally add the part of a that is *independent* of the temperature, viz. $a_\infty = a_1 + (a_2)_1$ according to (12), to the part that is dependent on the temperature according to (13^a), then we get at *high* temperature, taking $\omega = \frac{1}{2} \times (b_g)_\infty \times a$ into account (compare § XVI):

$$a = \frac{\omega}{n\,(1-n^2)} \left[(1-\varepsilon n)\,\tfrac{1}{4}\,\pi^2 + \frac{n}{1+n}\,\varphi \right] =$$

$$= \frac{1}{2n\,(1-n^2)}\,(b_g)_\infty\,a \left[(1-\varepsilon n)\,\tfrac{1}{4}\,\pi^2 + \frac{n}{1+n}\,\varphi \right],$$

or also

$$(\varphi \backsim 0) \qquad a = a_\infty \left[1 + \frac{n}{(1-\varepsilon n)\,(1+n)\,{}^1\!/_4\,\pi^2}\,\varphi \right] = a_\infty\,(1+\gamma\varphi)\,, \quad (14a)$$

in which therefore

$$a_\infty = \frac{{}^1\!/_4\,\pi^2\,(1-\varepsilon n)}{2n\,(1-n^2)}\,(b_g)_\infty\,a, \quad \text{and} \quad \gamma = \frac{n}{(1-\varepsilon n)\,(1+n)\,{}^1\!/_4\,\pi^2}.$$

We remind the reader of the fact that the coefficient ε (see § XVII) has the value 1 for $n = 1$, the value $8 : \pi^2 = 0{,}811$ for $n = 0$, and the value 0,845 for $n = 0{,}6$. Further $a = MN$, in which M is the maximum value of the function of force $f(r)$ at contact of the molecules, and N the total number of molecules in the volume v.

At *low* temperatures ($\varphi = \varphi_0 = 1 : k^2$) we get according to (13^b):

$$(\varphi \backsim \varphi_0) \qquad a = a_\infty \left[1 + \frac{log\ {}^1\!/_{n^2}}{{}^1\!/_4\,\pi^2\,(1-\varepsilon n)}\,log \frac{2}{\sqrt{1-k^2\,\varphi}} \right] \quad . \quad . \quad . \quad . \quad (14b)$$

That for $\varphi = \varphi_0$ the value of a becomes *logarithmically* infinite, and does not get near *exponentially* infinite, as is the case on assumption of BOLTZMANN's temperature-distribution factor (for $f(a) = (e^{a/RT} - 1) : a/RT$ becomes of the order e^{∞} for $T = 0$), is already to be esteemed an advantage. But the above found logarithmically infinite will lead to an ordinary *finite maximum*, when we consider that only the *very definite velocity* u_0, which causes φ to be $= M : \frac{1}{2}\mu u_0^2 = 1 : k^2$, leads to this *log* ∞. When we take MAXWELL's law of the *distribution of velocities into account*, the adjacent velocities will not lead to *log* ∞, and this will accordingly pass into a finite maximum. We shall come back to this later on.

We will, however, point out already here that the logarithmic infinity for $\varphi = \varphi_0$ is *not* bound to our special assumption (8) concerning $F(r)$. We shall see that this *log*-infinite value of a for $\varphi = \varphi_0$ is found on *any* supposition concerning $F(r)$.

But the numerical values of the quantities a_∞ and γ in (14^a) e.g. will of course be dependent on the said supposition. We possess a kind of control for the case $\varphi = 0, n = 1$. According to (14^a) a_∞ then becomes $= {}^1/_{16}\pi^2 \times (b_g)_\infty a$, because $(1 - \varepsilon n)$ then becomes $= 1 - n$, hence $(1 - \varepsilon n) : n(1 - n^2) = 1 : n(1 + n) = {}^1/_2$. But according to the ordinary (statical) theory, the attractive virial (see § IX) must be $= {}^2/_3 \pi N n \int_s^a r^3 \frac{dP_r}{dr} dr$. When $a = s$, $r^3 = s^3$ can be brought before the integral sign, and we have ${}^2/_3 \pi N n s^3 (P_r)_s^a = {}^2/_3 \pi N n s^3 (0 - (-M)) = {}^2/_3 \pi N s^3 \times MN : v$ (as $n = N : v$). Hence we find with $MN = a$ for a the value $(b_g)_\infty \times a$, so that the factor by which we have to multiply, would have to be $= 1$, and not $= {}^1/_{16}\pi^2 = 0{,}617$, as we have found. In my opinion this conclusion can only be drawn from it, that even in the limiting case $T = \infty$ $(\varphi = 0)$ the factor of distribution at the molecule surface (the sphere of attraction is infinitely thin on the assumption $a = s$) is not $= 1$, as we assumed above in the application of the statical method, but slightly less in consequence of the influence of the *passing* molecules, which does not disappear even for $n = 1$, which is the cause that the full maximum value M of the function of force is not reached. And the difference will depend on the nature of the function of force used.

For $n = 0{,}6$ the factor of $(b_g)_\infty a$ will get the value $\frac{2{,}467 \times 0{,}483}{1{,}2 \times 0{,}64} = \frac{1{,}192}{0{,}768} = 1{,}55$, which comes to this, that the attraction

might be thought concentrated at a distance $s\sqrt[3]{1,55} = 1,16\,s$ from the centre of the considered molecule (the sphere of attraction extends between s and $1,67\,s$ for $n = 0,6$).

We saw already that φ represents the quantity $M : {}^1/_2\,\mu\,u_0^2$. In this u_0 represents the mean relative velocity with which the molecules penetrate the sphere of attraction. But this velocity is augmented by a certain amount within the sphere of attraction, so that u_0 will not be in *direct* relation with the temperature. For *very large volumes* we may, however, entirely neglect this slight modification in the velocity in comparison with the much larger part of the path passed over with the velocity u_0. Only for small volumes this is no longer allowed, and in consequence of this new complications will make their appearance.

We may now write:

$$\varphi = \frac{M}{{}^1/_2\mu\,u_0^2} = \frac{MN}{{}^1/_2\mu\,Nu_0^2} = \frac{a}{2 \times {}^3/_2\,RT} = \frac{{}^1/_3\,a}{RT},$$

because the mean square of the *relative* velocity is twice that of the square of velocity U_0^2 itself, and ${}^3/_2\,RT$ may be written for ${}^1/_2\,\mu\,N\,U_0^2$. According to all that was developed above,

$$a = a_\infty\left(1 + \gamma_1\frac{{}^1/_3\,a}{RT} + \gamma_2\left(\frac{{}^1/_3\,a}{RT}\right)^2 + \cdots\right) \quad . \quad . \quad . \quad . \quad (15a)$$

may therefore be written for a, according to (14^a) — at least for not too low temperatures, and when also higher powers of φ are taken into consideration; whereas for *low* temperatures (φ near $\varphi_0 = 1 : k^2$) an expression of the form

$$a = a_\infty\left(1 - \lambda\,log\,{}^1/_2\sqrt{1 - \frac{\varkappa}{RT}}\right) \quad . \quad . \quad . \quad . \quad (15b)$$

will better answer the purpose, according to (14^b). In this $\varkappa = k^2 \times {}^1/_3\,a = \frac{n^2}{1-n^2} \times {}^1/_3\,a$, in which it should be borne in mind that the *log* is now negative, so that the minus sign before λ becomes positive again.

We have already pointed out before that the supposition of an *exceedingly* thin sphere of attraction, as is sometimes assumed, must be entirely excluded for several reasons [1]). To this comes the circumstance that for $n = 1$ the limiting temperature T_0, in which a will become logarithmically infinite (or at least maximum), is given by $\varphi_0 = 1 : k^2 = (1-n^2) : n^2$, which for $n = 1$ would give the value 0 for φ_0, i.e. $T = \infty$. And as it has been experimentally found that the said

[1]) Cf. our first paper.

maximum lies at very low temperatures (a continues namely to increase, for H_2 for instance, up to at least $^1/_2\ T_k$), the assumption $n = 1$ must be quite rejected.

As the value 0,08 (about) is found for $^1/_3 a$ with H_2, the value of $RT_0 = {}^1/_3\, a : \varphi_0$ would become $\frac{0{,}36}{0{,}64} \times 0{,}08 = 0{,}045$ with $n = 0{,}6$ (i. e. $s = {}^3/_5\, a$ or $a = 1{}^2/_3\, s$), i. e. T_0 about 12°,3 absolute. This is very well possible, as we have seen that for H_2 the value of a is still increasing up to 16° abs. (from $a_\infty = 370 \times 10^{-6}$ to $a_{16^0} = 740 \times 10^{-6}$ about). What is very remarkable, is the fact that the limiting temperature seems to lie so close to the *triple point* of H_2 (viz. 14° abs.).

Fontanivent, January 1918. (*To be continued*).

Physics. — "*On the Course of the Values of a and b for Hydrogen at Different Temperatures and Volumes*". IV. (Continued). By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of March 23, 1918).

§ XX. The value of a below the limiting temperature.

In this case the integrations need no longer take place in different stages, since a minimum distance r_m, which is dependent on θ, need no longer be reckoned with, so that first the integration with respect to θ can be carried out, and then with respect to r. All the entering molecules, from $\theta = 0$ to $\theta = 90°$, will now come in collision; for the limiting temperature T_0 the molecules that strike under an angle $\theta = 90°$ will just pass the rim of the molecule that is supposed not to move. We have, therefore, now to integrate (see § XVI):

$$a = {}^1/_2 \times (b_g)_\infty \alpha \times \frac{2a^4}{s\,(a^2-s^2)} \int_s^a \int_0^{{}^1/_2\pi} \frac{dr \times \sin\theta\, d\theta}{r\sqrt{a^2\cos^2\theta + (a^2-r^2)\,(k^2\varphi-1)}},$$

in which $k^2\varphi$ is now always > 1, and in the limiting case $\varphi = \varphi_0 = 1 : k^2$ assumes the value 1. When we put $(a^2-r^2)\,(k^2\varphi-1) = q^2$, we get therefore:

$$a = {}^1/_2 \times (b_g)_\infty \alpha \times \frac{2a^3}{s\,(a^2-s^2)} \int_s^a \frac{dr}{r} \int_{{}^1/_2\pi}^0 \frac{d\,(a\cos\theta)}{\sqrt{q^2+a^2\cos^2\theta}},$$

in which we may write for the second integral:

$$\log\,(a\cos\theta + \sqrt{q^2+a^2\cos^2\theta})_{{}^1/_2\pi}^0 = \log\frac{a+\sqrt{q^2+a^2}}{q},$$

so that we have still to integrate:

$$a = {}^1/_2 \times (b_g)_\infty \alpha \times \frac{2a^3}{s\,(a^2-s^2)} \int_s^a \frac{dr}{r} \log\left(\frac{a}{q} + \sqrt{1+\frac{a^2}{q^2}}\right) \quad . \quad (16)$$

If in the first place φ is near φ_0, then q approaches 0, and the integral approaches to

$$\int_s^a \frac{dr}{r} \log \frac{2a}{q} = \int_s^a \frac{dr}{r} \left[\log \frac{2}{\sqrt{k^2\varphi - 1}} - \log \frac{\sqrt{a^2 - r^2}}{a} \right],$$

because q is $= \sqrt{k^2\varphi - 1} \times \sqrt{a^2 - r^2}$. Hence we have for the integral:

$$\log \frac{2}{\sqrt{k^2\varphi - 1}} \log \frac{a}{s} - \int_s^a \log \frac{\sqrt{a^2 - r^2}}{a} \cdot \frac{dr}{r}.$$

We have for the last integral with $r : a = x$, $s : a = n$:

$$-\tfrac{1}{2} \int_n^1 \log (1 - x^2) \cdot \frac{dx}{x} = \tfrac{1}{4} \left(\frac{x^2}{1} + \frac{x^4}{4} + \frac{x^6}{9} + \ldots \right)_n^1 = \tfrac{1}{24} \pi^2 (1 - \varepsilon' n^2),$$

in which $\varepsilon' = 1$ for $n = 1$, and $6 : \pi^2 = 0{,}608$ for $n = 0$. For $\frac{1}{1} + \frac{1}{4} + \frac{1}{9} + \ldots = \frac{1}{6}\pi^2$, and $\frac{n^2}{1} + \frac{n^4}{4} + \frac{n^6}{9} + \ldots = n^2 \left(1 + \frac{n^2}{4} + \frac{n^4}{9} + \ldots \right)$ is $= \frac{1}{4}\pi^2$ for $n = 1$, and $= n^2$ for $n = 0$. (For $n = 0{,}6$ $\varepsilon' = 0{,}674$).

Hence we get finally:

$$\underline{(\varphi \gtrless \varphi_0)} \quad a = \frac{1}{2\pi (1 - n^2)} (b_g)_\infty \alpha \left[\frac{1}{12} \pi^2 (1 - \varepsilon' n^2) + \log \frac{1}{n^2} \log \frac{2}{\sqrt{k^2\varphi - 1}} \right]. \quad (17)$$

When we compare this with (14^b), where we found for values of φ in the neighbourhood of φ_0 (but $< \varphi_0$, while φ remains $> \varphi_0$ in (16)):

$$(\varphi \lessgtr \varphi_0) \quad a = \frac{1}{2n (1 - n^2)} (b_g)_\infty \alpha \left[\frac{1}{4} \pi^2 (1 - \varepsilon n) + \log^2 \frac{1}{n} + \log \frac{1}{n^2} \log \frac{2}{\sqrt{1 - k^2\varphi}} \right],$$

we observe with regard to the member that is independent of T, a discontinuity appearing at $\varphi = \varphi_0$. [We have added, for a comparison, to the first (finite) term the term $\log^2 \frac{1}{n}$, which was cancelled in § 18 in form. (13b) by the side of the infinitely large logarithmic term].

For $n = 1$ we find (with the factor $\frac{1}{1 - n^2}$ from the factor before the sign of integration) in the first case $\frac{1}{12}\pi^2 \frac{1 - n^2}{1 - n^2} = \frac{1}{12}\pi^2$, in the second case $\frac{1}{4}\pi^2 \frac{1 - n}{1 - n^2} + \log^2 \frac{1}{n} = \frac{1}{8}\pi^2$. And for $n = 0$ we find $\frac{1}{12}\pi^2$, resp. $\frac{1}{4}\pi^2 + \log^2 \frac{1}{n} = \frac{1}{4}\pi^2 + \infty^2$. This difference can be partly accounted for by the sudden disappearance at $\varphi = \varphi_0$ of the terms which refer

to the *passing* molecules, and which, therefore, do not occur any more in (17). But in any case the difference is of no importance, as these terms, which are independent of φ, remain finite with respect to the term that depends on φ, and logarithmically approaches infinity. (In the case $n = 0$, where — for infinitely large spheres of attraction — the entire quantity a would become infinite, and accordingly our derivation is no longer valid, the fact that $log^2 \frac{1}{n}$ becomes infinite, is of no importance at all).

We will still point out that for $\varphi = \varphi_0$ a does not only become logarithmically infinite with the form of $f(r)$ assumed by us, but with any arbitrary assumption about this. Compare for this Appendix C.

We suppose in the second place in (16) φ near ∞ (i.e. T near 0).

For the integral in (16) we may then write, as q becomes very large:

$$\int_s^a \frac{dr}{r} log\left(\frac{a}{q} + 1 + \tfrac{1}{2}\frac{a^2}{q^2}\right) = \int_s^a \frac{dr}{r} \times \frac{a}{q} = \frac{a}{\sqrt{k^2\varphi - 1}} \int_s^a \frac{dr}{r\sqrt{a^2 - r^2}},$$

i.e.

$$\frac{1}{\sqrt{k^2\varphi - 1}} \left(log \frac{a - \sqrt{a^2 - r^2}}{r}\right)_s^a = \frac{1}{\sqrt{k^2\varphi - 1}} \left(log\, 1 - log \frac{a - \sqrt{a^2 - s^2}}{s} = \right.$$

$$= \frac{1}{\sqrt{k^2\varphi - 1}} log \frac{a + \sqrt{a^2 - s^2}}{s}.$$

When the factor before the sign of integration is taken into account we get therefore:

$$\underline{\begin{pmatrix} \varphi \backsim \infty \\ T \backsim 0 \end{pmatrix}} \qquad a = \frac{1}{n(1-n^2)} \times (b_q)_\infty \alpha \times \frac{1}{\sqrt{k^2 q - 1}} log \frac{1 + \sqrt{1-n^2}}{n} \quad . \quad (18)$$

This approaches 0 therefore, when φ approaches ∞ (T approaches 0). We may write for $k^2\varphi - 1$, after substitution of the value for φ, the expression $\frac{n^2}{1-n^2} \frac{^1/_3 \alpha}{RT} - 1 = \frac{n^2}{1-n^2} \frac{^1/_3 \alpha}{RT}$, when T is near 0.

Hence after the *maximum* for a at $\varphi = \varphi_0$ the attraction steadily decreases, and *disappears* at 0° abs. This result was to be foreseen. In the original integral of the virial of attraction the radical quantity in the denominator becomes namely $= \infty$ at 0° abs., when φ becomes $= \infty$. This radical quantity expresses the relative increase of velocity in the sphere of attraction, and as this increase remains *finite* with respect to $u_0 = 0$, the *relative* increase will become infinitely great.

And this relative increase of velocity entirely determines the density in the sphere of attraction, which is in inverse ratio to it.

We observe once more here, that the earlier BOLTZMANN theory would give an *exponentially infinite* value for a at 0° abs., whereas in reality it is $= 0$.

For $n=1$ ($a=s$) the limiting value of $\frac{1}{1-n^2}$ will be $= log \frac{1+\sqrt{1-n^2}}{n} =$ $= \frac{1}{\sqrt{1-n^2}}$. With $\sqrt{\frac{n^2}{1-n^2}}$ in $\sqrt{k^2\varphi - 1}$ (see above) this becomes $1 : n$, so that then a will approach $(b_g)_\infty \alpha \times \sqrt{\frac{RT}{{}^1/_3\alpha}}$.

For $n = 0$ (a great with respect to s) the absolute zero coincides with the limiting temperature, given by $\varphi_0 = 1 : k^2 = (1-n^2) : n^2$. For then $\varphi_0 = \infty$ ($T_0 = 0$). In (18) $Lim \frac{1}{n} log$ becomes further $= \frac{1}{n} log \frac{2}{n}$, so that then a will approach $(b_g)_\infty \alpha \times \frac{1}{n} log \frac{2}{n} \times \frac{1}{\sqrt{n^2 \frac{{}^1/_3\alpha}{RT} - 1}}$, which again becomes $= 0$ for $T = 0$, so long as n is not absolutely $= 0$, which of course would be practically impossible.

Summarising we can therefore state, in agreement with the above developed exact theory concerning the quantity a for *very large volume*, that a, from a limiting value at $T = \infty$, steadily increases to a *maximum value* at $T = T_0$, after which it decreases again, till a has become $= 0$ at the absolute zero. The mentioned limiting temperature T_0 is then determined by $RT_0 = {}^1/_3 \alpha : \varphi_0$, in which $\varphi_0 = (1-n^2) : n^2$. ($n = s : a$, in which s represents the diameter of a molecule, and a the radius of the sphere of attraction). For H_2 T_0 is about $= \frac{1}{2} T_k$, the ratio of the values of a_∞, a_k, and a_0 being $1 : 1{}^1/_3 : 2$.

In the next paper we shall briefly discuss the influence of MAXWELL'S distribution of velocity, and then treat the course of the quantity b from $T = \infty$ to $T = 0$, likewise at large volume. Then the values of a and b for *small* volumes will be considered, so as to make a complete theoretical insight possible concerning the *whole* course of a and b along the boundary line, both along the vapour branch and along the liquid branch.

Fontanivent, January 1918. (*To be continued*).

APPENDIX.

A. The integral $k\int_0^{\frac{1}{2}\pi}\frac{\sin\psi}{\sqrt{1+k^2\sin\psi}}\psi d\psi$. (addition to § **XVII**).

When we expand this into a series through repeated partial integration, we get:

$$\int\frac{\sin\psi}{\sqrt{1+k^2\sin^2\psi}}\psi d\psi=\int P.\,\psi d\psi=\frac{\psi^2}{2}P-\frac{\psi^3}{6}\frac{dP}{d\psi}+\frac{\psi^4}{24}\frac{d^2\psi}{d\psi^2}-\frac{\psi^5}{120}\frac{d^3P}{d\psi^3}+..,$$

in which (through ψ) all the terms at the lower limit 0 disappear. And for the upper limit all the *odd* differential quotients of P will disappear, because in this $\cos\psi$ occurs as factor. Indeed, when we put $1+k^2\sin\psi=\omega$, so that $\frac{d\omega}{d\psi}$ becomes $=2k^2\sin\psi\cos\psi$, we have:

$$\frac{dP}{d\psi}=-\tfrac{1}{2}\frac{\sin\psi}{\omega^{3/2}}(2k^2\sin\psi\cos\psi)+\frac{\cos\psi}{\omega^{1/2}}=\cos\psi\left(\frac{-k^2\sin^2\psi}{\omega^{3/2}}+\frac{1}{\omega^{1/2}}\right)=$$

$$=\cos\psi\left(\frac{1-\omega}{\omega^{3/2}}+\frac{1}{\omega^{1/2}}\right)=\frac{\cos\psi}{\omega^{3/2}}.$$

$$\frac{d^2P}{d\psi^2}=-\tfrac{3}{2}\frac{\cos\psi}{\omega^{5/2}}(2k^2\sin\psi\cos\psi)-\frac{\sin\psi}{\omega^{3/2}}=-\sin\psi\left(\frac{3k^2\cos^2\psi}{\omega^{5/2}}+\frac{1}{\omega^{3/2}}\right)=$$

$$=-\sin\psi\left(\frac{3(1+k^2)}{\omega^{5/2}}-\frac{2}{\omega^{3/2}}\right),$$

because $k^2\cos^2\psi=k^2-k^2\sin^2\psi=k^2-(\omega-1)=(1+k^2)-\omega$. We have further:

$$\frac{d^3P}{d\psi^3}=-\sin\psi\left(\frac{15(1+k^2)}{\omega^{7/2}}-\frac{6}{\omega^{5/2}}\right)(-k^2\sin\psi\cos\psi)-\cos\psi\left(\frac{3(1+k^2)}{\omega^{5/2}}-\frac{2}{\omega^{3/2}}\right)$$

$$=-\cos\psi\left[\left(\frac{15(1+k^2)}{\omega^{7/2}}-\frac{6}{\omega^{5/2}}\right)(1-\omega)+\left(\frac{3(1+k^2)}{\omega^{5/2}}-\frac{2}{\omega^{3/2}}\right)\right]$$

$$=-\cos\psi\left(\frac{15(1+k^2)}{\omega^{7/2}}-\frac{12(1+k^2)+6}{\omega^{5/2}}+\frac{4}{\omega^{3/2}}\right).$$

And also:

$$\frac{d^4P}{d\psi^4}=-\cos\psi\left(\frac{105(1+k^2)}{\omega^{9/2}}-\frac{60(1+k^2)+30}{\omega^{7/2}}+\frac{12}{\omega^{5/2}}\right)(-k^2\sin\psi\cos\psi)+$$

$$+\sin\psi\left(\frac{15(1+k^2)}{\omega^{7/2}}-\frac{12(1+k^2)+6}{\omega^{5/2}}+\frac{4}{\omega^{3/2}}\right)$$

$$= \sin\psi \left[\left(\frac{105\,(1+k^2)}{\omega^{9/2}} - \frac{60\,(1+k^2)+30}{\omega^{7/2}} + \frac{12}{\omega^{5/2}} \right) ((1+k^2)-\omega) + \right.$$

$$\left. + \left(\frac{15\,(1+k^2)}{\omega^{7/2}} - \frac{12\,(1+k^2)+6}{\omega^{5/2}} + \frac{4}{\omega^{3/2}} \right) \right]$$

$$= \sin\psi \left[\frac{105(1+k^2)^2}{\omega^{9/2}} - \frac{60(1+k^2)^2+120(1+k^2)}{\omega^{7/2}} + \frac{60(1+k^2)+24}{\omega^{5/2}} - \frac{8}{\omega^{3/2}} \right].$$

Etc. Etc. As has been said, all the odd differential quotients disappear for $\psi = {}^1/_2\pi$, and as ω becomes $= 1 + k^2$ for $\psi = {}^1/_2\pi$, we keep:

$$\left(\frac{d^2P}{d\psi^2}\right)_{1/2\pi} = -\frac{1}{\omega^{3/2}} = -\frac{1}{(1+k^2)^{3/2}};$$

$$\left(\frac{d^4P}{d\psi^4}\right)_{1/2\pi} = \frac{15}{\omega^{5/2}} - \frac{12}{\omega^{3/2}} - \frac{6}{\omega^{5/2}} + \frac{4}{\omega^{3/2}} = \frac{9}{(1+k^2)^{5/2}} - \frac{8}{(1+k^2)^{3/2}} = \frac{1-8k^2}{(1+k^2)^{5/2}}.$$

For the sake of brevity we have only taken the part with $\sin\psi$ into account in the last calculation of the two differential quotients: that with $\cos\psi$ is namely $= 0$. I. e. of $\frac{d^2P}{d\psi^2}$ only the part $-\frac{\sin\psi}{\omega^{3/2}}$, and of $\frac{d^4P}{d\psi^4}$ only the part with $\sin\psi$ in the first of the three lines belonging to this. The other parts have every time been necessary for the determination of the next higher differential quotient. Proceeding, we should have found:

$$\frac{d^6P}{d\psi^6} = -\left(\frac{225}{(1+k^2)^{7/2}} - \frac{360}{(1+k^2)^{5/2}} + \frac{136}{(1+k^2)^{3/2}} \right) = -\frac{1-88k^2+136k^4}{(1+k^2)^{7/2}}.$$

The coefficients of the highest powers of $1 + k^2$ are in all these results resp. $= 1^2$, $(1 \times 3)^2$, $(1 \times 3 \times 5)^2$, etc. The sum of the coefficients is always $= 1$, $(9 - 8 = 1;\ 225 - 360 + 136 = 1)$. Hence we get now, taking into consideration that $k : \sqrt{(1+k^2)} = \frac{s}{\sqrt{a^2-s^2}} : \frac{a}{\sqrt{a^2-s^2}} = \frac{s}{a} = n$, and $(P)_{1/2\pi} = 1 : \sqrt{1+k^2}$:

$$k \int_0^{1/2\pi} \frac{\sin\psi}{\sqrt{1+k^2\sin^2\psi}}\,\psi\,d\psi = n\left[\frac{({}^1/_2\pi)^2}{2} - \frac{1}{1+k^2}\,\frac{({}^1/_2\pi)^4}{24} + \right.$$

$$\left. + \frac{1-8k^2}{(1+k^2)^2}\,\frac{({}^1/_2\pi)^6}{720} - \frac{1-88k^2+136k^4}{(1+k^2)^3}\,\frac{({}^1/_2\pi)^8}{40320} + \text{etc.} \right],$$

in which we may also write $1 - n^2$ for $1 : (1 + k^2) = (a^2 - s^2) : a^2$. The above series is convergent, as is easily seen from the structure of the factors $(1-8k^2) : (1 + k^2)^{5/2} = 9 : (1 + k^2)^{5/2} = 8\,(1 + k^2)^{5/2}$, etc.

For *large* values of k ($a = s$, i. e. $n = 1$) it converges very greatly, and rapidly approaches the first term, i. e. $n \times {}^1/_8\pi^2$.

For *small* values of k (near 0, i. e. a large with respect to s, $n = 0$) the series becomes:

$$n\,[\tfrac{1}{2}\,(\tfrac{1}{2})\pi^2 - \tfrac{1}{24}\,({}^1/_2\pi)^4 + \tfrac{1}{720}\,({}^1/_2)\pi^6 - \text{etc.}] = n\,(1 - \cos\tfrac{1}{2}\,\pi) = n.$$

For the two limiting cases $n = 1$ and $n = 0$ we, therefore, find back the same values as we had already found by direct integration in the text of § 17.

When $n = 0{,}6$, we get $1 - 8k^2 = 1 - 4{,}5 = -3{,}5$, $1 - 88k^2 + 136k^4 = 1 - 49{,}5 + 43{,}0 = -5{,}5$, $1 : (1 + k^2) = 0{,}64$, so that with ${}^1/_4\pi^2 = 2{,}4674$, the integral being put $= \varepsilon n \times {}^1/_8\,\pi$ (cf. the text of § 17), we find from

$$\varepsilon = 1 - \frac{1}{1+k^2}\frac{({}^1/_2\vartheta)^2}{12} + \frac{1-8k^2}{(1+k^2)^2}\frac{({}^1/_2\pi)^4}{360} - \frac{1-88k^2+136k^4}{(1+k^2)^3}\frac{({}^1/_2\pi)^6}{20160} + \text{etc.}$$

for ε the value

$$1 - 0{,}1316 - 0{,}02425 + 0{,}00107 \ldots = 0{,}8452 \ldots = 0{,}845.$$

B. The integral $k\int_{tg\vartheta_0:k}^{1} \frac{\cosh\psi}{\sqrt{1+k^2\cos^2 h\,\psi}}\,\psi d\psi$ (addition to § **XVIII**).

In entirely the same way as for the above treated integral we find through repeated partial integration:

$$k\int_{tg\vartheta_0:k}^{1} \frac{\cos h\,\psi}{\sqrt{1+k^2\cos^2 h\,\psi}}\,\psi\,d\psi = -\left[\frac{tg\theta_0}{\sec\theta_0}\frac{log^2}{2} - \frac{k\sqrt{\frac{tg^2\theta_0}{k^2}-1}}{\sec^3\theta_0}\frac{log^3}{6} + \right.$$

$$+ tg\,\theta_0\left(\frac{3(1+k^2)}{\sec^5\theta_0} - \frac{2}{\sec^3\theta_0}\right)\frac{log^4}{24} -$$

$$\left. - k\sqrt{\frac{tg^2\theta_0}{k^2}-1}\left(\frac{15(1+k^2)}{\sec^7\theta_0} - \frac{12(1+k^2)+6}{\sec^5\theta_0} + \frac{4}{\sec^3\theta_0}\right)\frac{log^5}{120} + \text{etc.}\right],$$

in which *log* represents $log\left(\frac{tg\theta_0}{k} + \sqrt{\frac{tg^2\theta_0}{k^2}-1}\right)$.

In this it has been taken into account that $d\cosh\psi = \sinh\psi$ and $d\sinh\psi = \cosh\psi$, and that further $-k^2\cos^2 h\,\psi$ can again be replaced by $1-\omega$ (when namely $1 + k^2\cos^2 h\,\psi$ is put $= \omega$) and $-k^2\sin^2 h\,\psi$ by $-k^2\cos^2 h\,\psi + k^2 = (1 + k^2) - \omega$. Now the terms with odd powers of ψ do *not* disappear, because at the lower limit the factor $\sinh\psi$, which occurs for these powers, does not disappear (as for the above

treated integral $\cos\psi$ at the upper limit), but becomes $= \sqrt{\frac{tg^2\theta_0}{k^2} - 1}$, because $\cosh\psi$ then is $= tg\theta_0 : k$. At the upper limit everything disappears, because then $\psi = 0$. (Besides, the terms with odd powers of ψ still contain the factor $\sinh\psi$, which now likewise becomes $= 0$, because $\cosh\psi$ becomes $= 1$ at the upper limit. (Cf. further the text of § 18)). We may, therefore, write:

$$k\int = -\left[\sin\theta_0\left\{\frac{log^2}{2} + \left(\frac{3(1+k^2)}{(1+tg^2\theta_0)^2} - \frac{2}{1+tg^2\theta_0}\right)\frac{log^4}{4} + \text{etc.}\right\} - \right.$$
$$- \sqrt{\frac{tg^2\theta_0 - k^2}{1+tg^2\theta_0}}\left\{\frac{1}{1+tg^2\theta_0}\frac{log^3}{6} + \left(\frac{15(1+k^2)}{(1+tg^2\theta_0)^3} - \frac{12(1+k^2)+6}{(1+tg^2\theta_0)^2} + \right.\right.$$
$$\left.\left. + \frac{4}{1+tg^2\theta_0}\right)\frac{log^5}{120} + \text{etc.}\right\}\Bigg].$$

Let us now introduce the quantity φ, determined by equation (6) of the last paper but one, viz.

$$\frac{a^2}{s^2}\sin^2\theta_0 = 1 + \frac{M}{{}^1/_2\mu u_0^2} = 1 + \varphi,$$

in which, therefore, φ depends on the *temperature* (determined by ${}^1/_2\mu u_0^2$). For $1 + tg^2\theta_0$ we may write $\frac{1-k^2\varphi}{1+k^2}$, because $k^2(1+\varphi) : (1-k^2\varphi)$ may be substituted for $tg^2\theta_0 = \frac{s^2}{a^2}(1+\varphi) : \left(1 - \frac{s^2}{a^2}(1+\varphi)\right)$ with $\frac{s^2}{a^2-s^2} = k^2$. For $tg^2\theta_0 - k^2$ we find $k^2(1+k^2)\varphi : (1-k^2\varphi)$, so that we get:

$$k\int = -\left[\frac{k}{\sqrt{1+k^2}}\sqrt{1+\varphi}\left\{\frac{log^2}{2} + \frac{(1-k^2\varphi)(1-3k^2\varphi)}{1+k^2}\frac{log^4}{24} + \text{etc.}\right\} - \right.$$
$$- k\sqrt{\varphi}\left\{\frac{1-k^2\varphi}{1+k^2}\frac{log^3}{6} + \left(\frac{(1-k^2\varphi)^2(9-15k^2\varphi)}{(1+k^2)^2} - \right.\right.$$
$$\left.\left. - \frac{(1-k^2\varphi)(8-12k^2\varphi)}{1+k^2}\right)\frac{log^5}{120} + \text{etc.}\right\}\Bigg]$$

in which

$$log = log\left(\frac{tg\theta_0}{k} + \sqrt{\frac{tg^2\theta_0}{k^2} - 1}\right) = log\frac{\sqrt{1+\varphi} + \sqrt{(1+k^2)\varphi}}{\sqrt{1-k^2\varphi}}.$$

Let us now examine, what are the limiting values to which the found integral approaches at high temperatures, and at low temperatures (φ near $\varphi_0 = 1 : k^2$).

At *high* temperatures ($\varphi = 0$) *log* draws near to $log\,1 = 0$, so that all the terms with high powers of *log* are cancelled by the

side of the first term, and besides the whole part with $k\sqrt{\varphi}$ disappears. That in this case only the first term with log^2 remains, follows also from this that $tg\,\theta_0 = k^2(1+\varphi):(1-k^2\varphi)$ approaches k for $\varphi = 0$, so that in case of equality of the limits of the original integral the factor $k\cos h\psi : \sqrt{1+k^2\cos^2 h\,\psi} = k:\sqrt{1+k^2}$ does not change between them (with respect to the log that becomes 0 at both the limits), and can accordingly be brought outside the integral sign.

At *low* temperatures (but higher than the limiting temperature T_0, determined by $\varphi_0 = 1:k^2$) the whole second part of $k\int$ will again disappear in consequence of the factor $1-k^2\varphi$, which approaches 0, whereas of the first part again only the first term with log^2 remains. In this case $\cos h\,\psi = tg\,\theta_0 : k = \infty$ at the lower limit, and the factor of $\psi d\psi$ in the integral can again be placed outside the integral sign at this limit, which now prevails since the log becomes infinite there. At the other limit the log is namely $= 0$.

With close approximation we may, therefore, write (n has been written for $k:\sqrt{1+k^2} = s:a$):

$$k\int = -\tfrac{1}{2}\,n\sqrt{1+q}\;log^2\frac{\sqrt{1+\varphi}+\sqrt{(1+k^2)\varphi}}{\sqrt{1-k^2\varphi}},$$

with neglect of all the terms with higher powers of log. Only at intermediary temperatures the omitted part can have any influence — but the difference brought about by this might possibly be made to disappear entirely on a somewhat modified assumption concerning $f(r)$ between a and s (see § XVI).

C. The quantity a for $\varphi = \varphi_0 = 1:k^2$. (addition to § XX). The original integral was (cf § 16):

$$\mathfrak{a} = \tfrac{1}{2}\times(b_g)_\infty\,a\times\frac{2a^4}{s(a^2-s^2)}\int_s^a\int_0^{1/2\pi}\frac{r(-f'(r))dr\times\sin\theta d\theta}{\sqrt{1-\frac{a^2}{r^2}\sin\theta+\varphi f(r)}}.$$

We may also write for the integral:

$$\int_s^a\int_{1/2\pi}^0\frac{r^2(-f'(r))\,dr\;d(a\cos\theta)}{\sqrt{r^2\varphi f(r)-(a^2-r^2)+a^2\cos^2\theta}} = \frac{1}{a}\int_s^a r^2(-f'(r))\,dr\,log\left(\frac{a}{q}+\sqrt{1+\frac{a^2}{q^2}}\right),$$

when $r^2\varphi f(r)-(a^2-r^2) = q^2$ is put. When $f(r)$ is generally $= \frac{s^t}{r^t}$, so that this duly becomes $= 1$ for $r = s$, then $-f'(r) = \frac{ts^t}{r^{t+1}}$ and $q^2 = \frac{\varphi s^t}{r^{t-2}} - (a^2-r^2)$. Hence we now have:

$$\mathfrak{a} = (b_g)_\infty \alpha \times \frac{t a^3 s^{t-1}}{a^2 - s^2} \int_s^a \frac{dr}{r^{t-1}} log\left(\frac{a}{q} + \sqrt{1 + \frac{a^2}{q^2}}\right),$$

in which the quantity q for the lower limit passes into $\varphi s^2 - (a^2 - s^2)$, which becomes $= 0$ for $\varphi = \frac{a^2 - s^2}{s^2} = \frac{1 - n^2}{n^2} = \frac{1}{k^2}$ as before. The value of a will, therefore, again approach to *logarithmically infinite* for $\varphi = \varphi_0 = 1 : k^2$. This is, accordingly, entirely independent of the exponent t in the assumed law of force $f(r) \therefore r^{-t}$.

Physiology. — *"On the Peripheral Sensitive Nervous System."* By Dr. G. C. HERINGA. (Communicated by Prof. J. BOEKE).

(Communicated in the meeting of February 23, 1918).

When we endeavour to summarize our knowledge of the peripheral sensitive nervous system, which is a time-consuming experience as it involves the perusal of an enormous number of periodicals, we shall find amidst a mass of controversial matter a number of facts received by various controversialists, which, when put together, make up a gratifying whole.

In the neurological clinic the doctrine of neurons in still all but paramount, but in the neuro-anatomic literature it is quite a different thing. There, in spite of this same doctrine of neurons, experiences come to the front pointing to the existence of a very extensive continuous retiform structure of sensory nerves close to the periphery. As has been insisted upon by APATHY there exists a highly delicate texture of anastomotic nerve-fibers close under the surface of the body of invertebrates. This view has hardly been disqualified. It is now getting more and more evident that such a network is also to be found in vertebrates.

Many data regarding the "rete amielinica subpapillare" we owe especially to RUFFINI and his school, who based upon them his theory of the "circuito chuiso delle neurofibrille." According to the descriptions given by RUFFINI himself, the fibers of this network spring from different sources:

1. end-branches of the ordinary medullated fibers;
2. ultraterminals of endorgans;
3. sympathetic fibers;
4. ultraterminals of fibers belonging to the TIMOFEEW-system.

From all sides (BOTEZAT, LEONTOWITCH, PRENTISS, SFAMENI, DOGIEL) much evidential matter tending in the same direction, has been brought forward, so that no room is left for any doubt as to the principal facts, though there remains some difference of opinion regarding the components of the network, and though several inquirers will not go the length of subscribing to all the inferences of RUFFINI's "teoria unitaria."

Two recent publications from the Italian school seem to me to be

interesting in this connection. STEPHANELLI [1]) describes an extensive network of nerve-fibers, which he found in the skin of reptiles. This network built up of non-medullated fibers is easily distinguishable from the familiar subepithelial *plexus*, which lies deeper and in which only an interlacement of nerve-fibers, for the greater part still medullated, takes place. The relations of the non-medullated network to the subepithelial plexus are also described minutely by him. In the former, which spreads diffusely as a true network of nerves in the skin, he describes by the side of very few other endings an "organo di senso in stato diffuso," a conception which is the more plausible since the network is immediately connected with an intrapapillary extension of the same nature.

Here lies the link that joins STEPHANELLI's publication to that of VITALI. [2])

VITALI examined the skin of the nail-bed also after RUFFINI's gold-chloride method. His results correspond completely with those of similar researches by RUFFINI and others. In succession he describes the presence of many free endings easy to differentiate by the very melodious Italian names: gomitoli, alberelli, espansioni ad anse avoiticciati, fiochetti papillari, grappoli, and also of RUFFINI's, MEISSNER's and VATER-PACINI's corpuscles. The principal interest now hinges about the fact that he lays particular stress upon the occurrence of anastomoses between the terminals reciprocally and upon their contact, as a whole, with the rete amielinica subpapillare, therewith emphasizing the importance attached by RUFFINI long since to the ultraterminals as expounded in his teoria unitaria previously mentioned. Finally VITALI comes to the conclusion that all those terminals together with the rete subpapillare form one connected amyelinic meshwork. When following up the Italian school a little further, we shall see that this meshwork must be placed on a level with STEPHANELLI's diffuse network. Then also the various endorgans of the higher vertebrates will be found to be points of differentiation amidst less developed surroundings. "Eche cos'altra sono," as Simonelli puts it rhetorically, "quello che noi denomigniano espansioni, se non il condensarsi in punti limitati di un simile reticolo diffuso periferico: in altri termini se non punti nodosi e

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[1]) AUGUSTO STEPHANELLI. Nuovo contributo alla cognoscenza della espansioni sensitivi dei Rettili e considerazioni sulla tessitura del sistemo nervoso periferico. Intern. Monatschrift. f. Anat. u. Phys. XXXII 1916. — Sui dispositivi micros copici della sensibilita cutanea a nella mucosa orale dei Rettili. (Ibid. XXXII 1916).

[2]) G. VITALI. Contributo allo studio istologico dell unghia. Le expansioni nervose del derma sotto ungeale dell' uomo. (Ibid. XXXII 1915).

maglie piu serrati di una rete generale, che intimamente involge e compenetra i tessuti, per meglio localizzare e precusare gli stimoli periferici?"

Thus, according to this view an unbroken series of anastomoses must be traceable in numerous varieties of free endings from the rete amielinica on the one side to the tactile corpuscles inserted in a rete intrapapillare on the other.

It would perhaps be premature to consider this highly pregnant hypothesis as proven. Still, undoubtedly it is equally true that anyone who will take the trouble to look into the literature, will find attestations from other authors also pointing unmistakably in the same direction. It is evident that the border-lines demarcating the various forms of end-organs, classified into various groups, are by no means established. Nearly coeval with the study of the end-organs itself are the efforts to establish a phylogenetic pedigree of the various end-organs, in which the intricate forms are reduced to more primitive types (MERKEL, KRAUSE, and others). Certain it is also that the more forms are brought to light by modern researchers, the more the border-lines between the various groups are fading out.

With this we are impressed forthwith when looking at the illustrations accompanying the several publications (see e.g. CECCHERELLI [1]) v. D. VELDE). [2]) The leading modern authors (BOTEZAT, DOGIEL, SFAMENI and followers of RUFFINI) endeavour to demonstrate anastomoses between the various endings. DOGIEL [3]) says in his article about nerve-endings in the external genitalia: "Wenn wir die Beschreibung der Nervenendigungen in den verschiedenen Nervenapparaten, den Genitalkörperchen, den Endkolben und den Meissnerschen Körperchen, welche in der Haut der äusseren Genitalorgane gelegen sind, vergleichen, und zugleich die beigegebenen Zeichnungen betrachten, so müssen wir zu dem Schluss kommen, dasz zwischen ihnen kein wesentlicher Unterschied besteht".

SFAMENI [4]) also describes the relationship between the genital corpuscles and KRAUSE's end-bulbs, GOLGI-MAZZONI's corpuscles and VATER-PACINI's corpuscles on the one side and RUFFINI's corpuscles on the other.

BOTEZAT [5]) has written a long and comprehensive paper on the system and the interrelationship of the nerve-endorgans.

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[1]) Intern. Monatschr. XXV 1908.
[2]) Intern. Mon. XXVI 1909.
[3]) Arch. Micr. Anat. XLI.
[4]) Arch. di fisiol. I 1904.
[5]) Zeitsch. Wiss. Zool. LXXXIV. 1906.

But what seems to me to be more important than all this, as it falls in with RUFFINI's views, is that also the border-lines between the corpuscles and the "free" endings are gradually falling away. Here the only differential diagnostic is whether or not a capsule is present. The same characteristics of the nerve-fibers, of the supporting tissue, "tactile-cells" or whatever name may be given to the cells found in the endorgans are equally peculiar to either group of end-organs. This may be gathered from the illustrations and the descriptions in all papers. BOTEZAT makes particular mention of this, adding that a capsule round a nerve-ending is not a question of vital importance for it, either functionally or morphologically. On the contrary BOTEZAT very often finds by the side of a capsuled ending its fellow deprived of a capsule. Thus the free "Knäuel" are found side by side with the capsuled "Knäuel" and the bulbs of KRAUSE; side by side with MERKEL's cells GRANDRY's and MEISSNER's corpuscles etc. Moreover, BOTEZAT distinguishes all sorts of gradations between the free and the capsuled endings.

In other authors we find the same again. RUFFINI's corpuscles are according to VITALI [1]) nothing else but capsuled "alberelli".

DOGIEL [2]) also speaks of non-capsuled corpuscles of RUFFINI. SFAMENI [3]) asserts that non-capsuled varieties occur of the same Genital corpuscles, which, as has been observed, are allied to all sorts of tactile-corpuscles. Of MEISSNER's corpuscles there seems to exist a large variety of simple modifications.

SFAMENI describes intermediate forms between MEISSNER's corpuscles and "fiochetti papillare" i. e. free endings. DOGIEL's modifications of MEISSNER's corpuscles (RUFFINI calls them DOGIEL's corpuscles) are non-capsuled at the upper-pole from which the axis-cylinders are branching off into free endings. They are types of RUFFINI's "espansioni misti". Other modifications again of MEISSNER's corpuscles (DOGIEL, v. D. VELDE) are characterised by their having a slightly developed capsule and a simplified nervecourse. DOGIEL's "eingekapselte Knäuel" described by him in 1903 as modified MEISSNER's corpuscles must therefore be closely allied to the free endings, perhaps identical with them (see supra). It seems, then, that MEISSNER's corpuscles are, in a higher degree than many other forms, closely allied to free nerve-endings. So when observing the several findings concerning the capsule of these corpuscles, we shall see that LAN-

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[1]) Int. Mon. XXXI. 1915.

[2]) Arch. f. Micr. Anat. 1903.

[3]) l.c.

GERHANS [1]) absolutely disproves its existence. He says: "Es besitzt *der Zellhaufen* [2]) den man Tastkörper nennt, nicht einmal eine eigene umschliessende Membran. Ueberal stossen die peripheren Zellen direct an das umgebende Bindegewebe, und nur nach längerer Einwirkung eines Reagenzes kann es vorkommen, dasz das starre Aussehen der Bindegewebsschichten eine eigene Membran vortäuscht".

Likewise ROUGET, TAFANI, IZQUERDO, HOGGAN, LEONTOWITCH absolutely deny the existence of a capsule. MEISSNER, RENAUT, KRAUSE, WOLFF, KOLLMAN and LEFEBURE consider it as a single endothelial membrane. LEFEBURE [3]): "une simple lume conjoncture doublée sur une face profonde par un feuillet endothelial". From all this it follows that the hypothesis brought forward by DOGIEL, RUFFINI, THOMSA and KOLLIKER that the corpuscles are provided with a true lamella-capsule, is hardly tenable. The very gradations (and they are many) between MEISSNER's corpuscles and the free endings go far to substantiate a priori the opinion of LANGERHANS, who appears to have studied the organs under consideration thoroughly. They also support BOTEZAT's view when he puts MEISSNER's corpuscles on a level with the complicate, non-capsuled MERKEL's corpuscles. In virtue of my personal inquiry I incline to LANGERHANS's view, as will appear lower down.

Finally let us bestow consideration upon the problem of the genetic connections between the free endings and the tactile bodies with the subpapillary network.

If we confine ourselves to the more modern authors, we mention the names of BETHE, PRENTISS, BOTEZAT, LEONTOWITCH, SFAMENI and DOGIEL [4]), who have, all of them, discussed more or less minutely the subepithelial network and its connections with the nerve-endorgans.

BOTEZAT differs from the other investigators in that he considers the network to be independent of tactile corpuscles. This follows from his opinion that the rete amielinica, is built up of fibers of the so-called 2^{d} sort [5]). But for the rest, he sides with the Italian School,

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[1]) Arch. f. Micr. Anat. IX 1873.

[2]) The italics are mine.

[3]) Revue gen. d'histol. 1909.

[4]) BETHE. Allgemeine Anat. und Phys. des Nervensystems. Leipzig 1903
PRENTISS. Journ. of Comp. neur. XIV 1904.
BOTEZAT l.c.
LEONTOWITCH Int. Mon. XVIII 1901.
SFAMENI, DOGIEL l.c.

[5]) Medullated fibers losing their myelin already in the nerve-trunk. It seems doubtful whether these fibers are still to be considered as a separate group.

our starting point, when in speaking about certain free endings, he says that through anostomoses they form a widely spread end-structure, "welcher in der Form eines im allgemeinen weitmaschigen varikösen Netzes von weithin ausgebreiter Ausdehnung erscheint", which continues into the papillae, and there adheres to ordinary medullated fibers. He looks upon this nerve-complex as a "für sich bestehender sensibeler Apparat der Lederhaut". He finds it again in fishes and amphibia, so it is beyond doubt that he describes the very network which STEPHANELLI discusses in his publication.

DOGIEL, an authority on end-organs, concurs with RUFFINI that the lateral branches of the free papillary endings blend with the rete amielinica: "Wie aus dem mitgeteilten hervorgeht, so hat das aus Marklosen Aestchen und Faden zusammengesetzte subpapillaire Nervengeflecht, die uneingekappselte Nervenknäuel sowie die Schleifenförmig gebogene Bündel und das intrapapillaire Fädennetz einen und denselben Ursprung". Also the TIMOFEEW fibres of the MEISSNER-corpuscles, which DOGIEL reckons among the sensory system, go to make up according to him, the intrapapillary nerve-complex by means of their ultraterminals.

SFAMENI, though far from adhering to the teoria unitaria gives a description of the subepithelial plexus and of its connection with tactile corpuscles and free endings, that accords fairly with RUFFINI's. Nor is it on the whole contradicted by PRENTISS and LEONTOWITCH in their publications respectively of Rana and the human skin.

It surely will not do to ignore the many differences between the various authors, differences in theoretical conception, in appreciation and in interpretation of their observations. Opposed to DOGIEL, who still holds that interlacement of the fibers is the fundamental principle governing the structure of the network, are BOTEZAT, BETHE, RUFFINI, LEONTOWITCH, and SFAMENI, who are convinced of the fusion of the fibers. PRENTISS wavers. It is a fact that the network is built up of sensitive fibers. However, the question whether also sympathetic elements are fused with it, is as yet unsettled. This depends in some degree on the doubtful character of the TIMOFEEW fibers. Still, though the origin of the sensory part of the network is still uncertain, there is no denying that, also in this respect, observers concur more and more. As we observed before BOTEZAT considers the whole network to be made up of anastomotic free nerve-endings. DOGIEL also looks upon them as the principal components, but according to him also ultraterminals of the TIMOFEEW system of the tactile corpuscles unite with it. SFAMENI believes there is *also* some connection with the genital corpuscles; LEONTOWITCH, BETHE, and PRENTISS assume an

immediate connection of the network with the free endings as well as with corpuscles. All these authors, though theoretically far removed from RUFFINI's neurogenetic conceptions, have brought forward a number of facts corresponding satisfactorily with those insisted upon most emphatically by the Italian school.

In short there is in the literature about the subject a tendency towards the hypothesis that there is, generally speaking, interconnection and coherence in the whole peripheral sensory nervous system.

It is these facts, derived from the literature, that enhance the significance of recent personal studies made by the BIELSCHOWSKY method on the sensory nerve-endings.

The BIELSCHOWSKY method differs from the methylene blue- and the gold-chloride method in that it affords another view of the problems. It does not present those typical appearances, which, when comparatively slight magnifications of rather thick sections are examined, yield a clear survey of the relations. Its efficiency lies in the fact that when preparations counterstained in haem. eosin, are examined under a microscope of the highest power, it brings out in strong relief the relations between the fibrils and their surroundings.

Along this totally different path I arrived at conclusions which, as I hope, will contribute to lend support to the hypothesis that the MEISSNER corpuscles are more related to the free endings than is commonly believed.

In a paper read at last year's Congress for Physics und Medicine at The Hague (1917) (see also: Verslagen Kon. Ak. v. Wetensch. 27 April 1917) I recorded some morphological data, hitherto unknown, concerning the structure of the axis-cylinder. In that paper I set forth that, when tracing an ordinary nerve-fiber from centre to periphery, the following changes in the structure are to be observed in a transverse section. First we find in the medullary sheath the axoplasm, which (in a transverse section) seems to be vacuolar in structure and embraces the neurofibrils in the protoplasmatic septa between the vacuoles. As known, the medullary sheath is surrounded by the protoplasmatic sheath of SCHWANN with its nucleus. More towards the periphery the medullary sheath splits up into several tubes. The always vacuolar axoplasma material with its fibrils spreads over the daughter medullary sheaths. Together they remain embedded in one undivided protoplasmatic mass, which must be considered as a continuation of the sheath of SCHWANN. Still further towards the terminus of the course of the nerve the medullary sheaths disappear from the section, so that the neurofibrils lie free in the protoplasmatic envelopment which, now being of vacuolar structure like

the primitive axis-cylinder, must be assimilated to the sheath of SCHWANN blended with the axoplasm. These formations are seen to get thinner and thinner and their meshes to get ever wider according as they approach the terminus of the nerve. To all appearance they ultimately blend or unite with the connective tissue plasmoderms in which we find the neurofibrils in the ultimate tract of their course [1]).

At first I was disposed to think that the described vacuolar dissolution of the axis-cylinder was characteristic of the so-called free nerve-endings, because I saw the medullated nerves force their way into the MEISSNER corpuscles without having undergone any modification.

I can go a step farther this time, and assert on the basis of a profound investigation of MEISSNER's corpuscles that the axis-cylinders inside these corpuscles pass through precisely the same disintegration process, previously described by me for the so-called free nerve-endings, and just now designated as a vacuolar dissolution.

Whereas nowadays it is maintained by many inquirers that the axis-cylinder loses its medullary sheath, before it enters into the corpuscles, I side with ENGELMANN [2]), LANGERHANS, FISCHER [3]) KEY—RETZIUS [4]) and LEFEBURE [5]), having been able to ascertain, in preparations treated with Osmic acid, that the medullary sheath, just as the sheath of SCHWANN, is prolonged into the intracorpuscular course of the nerves. Moreover my preparations also proved distinctly that those medullary sheaths split up inside the sheath of SCHWANN exactly as has been indicated above.

I hold with LEFEBURE that most likely the fact that the Osmium method has been abandoned for the modern fibril staining methods, is responsible for the erroneous opinions about the presence or the absence of medullary sheaths, prevailing in the neurological literature.

As to the sheath of SCHWANN, it goes without saying that I must contest the hypothesis that it passes into the formation of the capsule, since to me it is an intrinsic part of the lemmoblastic sheath. (DOGIEL and others [6])). My preparations, which are well impregnated and of good fixation also enable me to ascertain the fate of the axiscylinders

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1) Cf. J. BOEKE. Studien zur Nervenregeneration I, Verh. Kon. Ak. v. Wet. A'dam 2e Sectie Deel, XVIII n°. 6.

2) Zeitschr. Wiss. Zool. XII 1863.

3) Arch. f. Mikr. Anat. XII.

4) Arch. f. Mikr. Anat. IX 1873.

5) Revue génér. d'histologie 1909.

6) With more justice LANGERHAUS, KRAUSE and others assert that the sheath of SCHWANN passes into the inner capsule of the corpuscles.

inside the MEISSNER corpuscles. For among the cells filling up the core of the MEISSNER-corpuscles we find many of the same vacuolar non-medullated nerve-sections, which we have described, with the fibrils, scattered over the spongy protoplasm.

Now it was but another step to establish in well-chosen objects that those vacuolar axis-cylinders maintain their course in the cells of the core itself. In tangential sections we were in a position to observe with absolute certainty that from the axis-cylinder the fibrils pass *into* the protoplasm of those cells, where they may aid in making up a regular network of the fine fibrils, and where, as a continuation of the vacuolar structure of the axis-cylinder in transverse section, a reticular protoplasm serves as a substratum to the neurofibrils. Just as I observed previously in the corpuscles of GRANDRY, I saw also here a similar diffuse expansion of the network over the cell-protoplasm, as well as the mechanical traction phenomena between protoplasm and fibril-system, so that my interpretation leaves hardly any room for doubt. It is beyond all question that the core cells are indeed parts of the nerve-course itself; consequently it fits in with my view [1]) to term them lemmoblasts *together with* the other elements, building up the course of the nerve. The fibrillar networks described, are by no means terminal. As a rule the fibrils are seen to unite again and pursue their way as a new axis-cylinder. This is an additional argument for classing those cells among the structural elements of the nerve-course itself. In this way I came to the conclusion that *the entire* MEISSNER *corpuscle is built up of compact lemmoblast cords in structure completely similar to the free nerve-endings.* Now this appears to me to be an important conclusion, the more so when correlated with the above data regarding the connection between the tactile corpuscles and the free endings, as discussed in the literature.

In conclusion I will impart that in the MEISSNER corpuscles I found hardly anything that reminded me of a capsule, certainly not a fine fibrillary texture proper, still less a lamellar system. The enveloping connective tissue is rather of a loose spongy structure. I found in it vacuolar nerve-sections as well as "free" fibrils invested in the plasmoderms. I often descried that the contours of MEISSNER-corpuscles are very indistinct. Especially in the tactile balls of the cat's paw I rarely found typical MEISSNER corpuscles; often, however, in the papillary connective tissue I found detached groups

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[1]) Cf. G. C. HERINGA. Le développement des corpuscules de GRANDRY et de HERBST (Arch. néerl. des Sc. Exactes et nat. Serie III B. tome III 1917).

of nerve-sections of the familiar appearance in various sizes. Together they presented precisely the appearance of a transverse section of a MEISSNER corpuscle. Only by studying serial sections it can be ascertained whether we have to do with a MEISSNER corpuscle or rather with some detached axis-cylinders of free endings. Such forms, which must no doubt be classed as modified MEISSNER corpuscles, are in my judgment, as many proofs of the close relationship there is indeed between tactile corpuscles and free endings.

My conclusions, therefore, are the following:

1. the cells found by all inquirers [1]) except DOGIEL in the MEISSNER corpuscles are elements of the nerve-course itself, lemmoblasts, as I have endeavoured to demonstrate for GRANDRY-corpuscles.

2. As to structure and behaviour, the nerves in the MEISSNER-corpuscles correspond exactly with those of the so-called free-endings.

3. so that it is very likely that the terminal branches of the MEISSNER corpuscles (ultraterminals) form one connected whole with the free papillary endings.

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[1]) THOMSA. LANGERHANS, RANVIER, MERKEL, KRAUSE, LEONTOWITCH. SFAMENI, RUFFINE, LEFEBURE, VAN DE VELDE and others.

Astronomy. — *"On the Parallax of some Stellar Clusters"* (Second communication). By Dr. W. J. A. SCHOUTEN. (Communicated by Prof. J. C. KAPTEYN).

(Communicated in the meeting of February 23, 1918).

In a former communication it was shown, how it is possible to determine the parallaxes of stellar clusters from the numbers of stars of determined magnitude in the clusters by means of the luminosity curve of KAPTEYN. The calculation was performed for *Messier* 3 and *h and χ Persei*. Now the same method is used in order to determine the parallax of some other clusters.

The Small Magellanic Cloud.

H. S. LEAVITT. 1777 Variables in the Magellanic Clouds. Annals Harvard Observ. Vol. 60, N°. 4.

A preliminary catalogue containing 992 stars of the Small Cloud and 885 of the Great Magellanic Cloud. The places of 28 stars of catalogues in the neighbourhood of the Small Cloud are also given.

We counted a number of stars and estimated their diameter on a photographic plate, taken at the Harvard Observatory. For orientation we used the catalogue-stars the position of which Miss LEAVITT communicates. In order to reduce the estimates of diameters to magnitudes, we

1^{stly} counted an area of 1000 □′ without the Cloud, and determined from the numbers of stars of every magnitude the magnitude corresponding to every diameter by means of Publ. Gron. N°. 27, Table IV,

2^{ndly} we estimated the diameters of 142 variable stars, the magnitudes of which occur in LEAVITT's catalogue and which are equally distributed over the Cloud, and we have compared these with the mean magnitude, i. e. the average of maximum and minimum, given by Miss LEAVITT,

3dly we have estimated the diameters of the catalogue-stars mentioned above and compared these with the magnitudes in the C. P. D. and the A. G. C.

Finally the magnitude corresponding to each diameter was determined from all these data by graphical smoothing.

We counted an area of 240 □′ in the Cloud. The results are given in the table below. In it N_m represents the number of stars from the brightest star to the magnitude under consideration.

Diameter	Magn.	N_m	Magn.	N_m	A_m	Normal	Cluster
25	10.1	1	10.0	1	1	1	—
22	10.4	2					
20	10.7	4	10.5	4	3	—	3
17	11.2	5	11.0	5	1	1	—
16	11.3	6					
15	11.5	13	11.5	16	11	1	10
14	11.7	19					
13	12.0	26	12.0	33	17	1	16
12	12.2	39					
11	12.5	55	12.5	60	27	3	24
10	12.8	87					
9	13.1	122	13.0	122	62	4	58
8	13.4	172					
7	13.7	220	13.5	202	80	5	75
6	14.0	282	14.0	305	103	8	95
5	14.3	358					
4	14.6	467	14.5	438	133	11	122
3	14.9	568					
2	15.2	810	15.0	655	217	16	201
1	15.6	1104	15.5	1064	409	22	387
0	16.0						

The normal number of stars is calculated for the galactic latitude $b = 10°$. As we always use the luminosity curve for whole numbers as values of the argument m and have counted here by half magnitudes, we may deduce from the above table the following two tables:

m	A_m	A_{m+1} / A_m	m	A_m	A_{m+1} / A_m
12.0	33	3.24	11.5	18	3.39
13.0	107	1.81	12.5	61	2.48
14.0	194	2.35	13.5	151	1.79
15.0	455		14.5	270	

The irregular progress of the quotients $\frac{A_{m+1}}{A_m}$ is partly to be explained from our counting only a small part of the cluster.

These numbers give the following values for the parallax:

I	$\pi = 0''.0004$
II	4
III	7
IV	13
V	11
VI	4
Mean	$\pi = 0''.0007 \pm 0''.0002$

From 142 cluster variables that are equally distributed over the cluster and occur in Miss LEAVITT's catalogue, we find for the mean apparent magnitude of these stars $\overline{m} = 14.67$ and $5 \log. \pi = -15.77$, so that the mean absolute magnitude of these δ Cephei variable stars with a short period is $\overline{M} = 3.9$ according to our determination of the parallax.

From some δ Cephei variable stars with a long period HERTZSPRUNG found for the parallax of the Small Magellanic Cloud $\pi = 0''.0001$.

Praesepe.

$\alpha_{1900} = 8^h 34^m 39^s$, $\delta_{1900} = +20°1'$, $b = +33°$, $l = 169°$.

Dr. P. J. VAN RHIJN. The proper motions of the stars in and near the Praesepe cluster, Publ. Groningen, N°. 26, 1916.

The measurement of 2 sets of plates, taken at Potsdam. The catalogue contains 531 stars. The diameters were reduced to photographic magnitudes by means of standard magnitudes, determined by HERTZSPRUNG. The probable error of a magnitude is $\pm 0^m.12$.

We have derived the visual magnitudes from the photographic ones in the same way as VAN RHIJN did on page 10 of his publication. The correction was determined from the value of the colour

index for each *apparent* magnitude that is based on PARKHURST and SEARES' researches. To this objections may be raised, as for the cluster stars we have to deal with *absolute* magnitudes. As, however, the relation between colour index and luminosity is only inaccurately known as yet and as moreover, it cannot be decided whether a given star belongs to the cluster or not, VAN RHIJN's method is the only one possible. VAN RHIJN found that the photographic magnitudes (international scale) between $m = 7.5$ and $m = 14.5$ wanted a constant correction $-0^m.5$ for reduction to the visual Potsdam scale. Therefore by a correction $-0^m.7$ they are reduced to the Harvard scale.

The number of cluster stars of each magnitude we find by diminishing the numbers counted by the normal number, which was determined for this cluster from Publ. Gron. N°. 27, Table V.

It appears at once that the Praesepe stars have faint luminosities. The declivities that we observe in the frequency curve of the magnitudes are partly smaller than the smallest declivity occurring in KAPTEYN's luminosity curve. That is why we could make only four determinations of the parallax notwithstanding the great interval of magnitudes. These give

$$\pi = 0''.024 \pm 0''.004.$$

This parallax is considerably greater than the one which we found for other stellar clusters.

Messier 52.

N. G. C. 7654; $\alpha_{1900} = 23^h19^m.8$, $\delta_{1900} = +61°3'$, $b = +1°$; $l = 81°$; class: $D\,3$.

F. PINGSDORF. Der Sternhaufen in der Cassiopeia. Diss. Bonn. 1909. Measurements of three plates, taken by KÜSTNER. The catalogue contains 132 stars up to $15^m.0$. The standard magnitudes have been determined by visual observations by means of gauzes of 25 stars by ZURHELLEN.

We find from 4 determinations:

$$\pi = 0''.002 \pm 0''.0003.$$

Messier 46.

N. G. C. 2437; $\alpha_{1900} = 7^h\ 37^m.2$, $\delta_{1900} = -14°35'$, $b = +6°$, $l = 200°$; class: $D1$.

W. ZURHELLEN. Der Sternhaufen Messier 46. Veröffentl. Kgl. Sternwarte zu Bonn, N°. 11, 1909.

Measurements of three plates, taken by KÜSTNER. The catalogue

contains 529 stars. For standard magnitudes 47 stars were used, the brightness of which was estimated by KÜSTNER or determined by means of gauzes by ZURHELLEN.

We find from 4 determinations:

$$\pi = 0''.002 \pm 0''.0001.$$

Messier 37.

N. G. C. 2099; $\alpha_{1900} = 5^h45^m.8$, $\delta_{1900} = +32°31'$, $b = +4°$, $l = 145°$; class: $D1$.

J. O. NORDLUND. Photographische Ausmessung des Sternhaufens Messier 37. Inaug. Diss. Upsala 1909, Arkiv för Matematik, Astronomie och Fysik, Band 5, N°. 17.

Dr. H. GIEBELER. Der Sternhaufen Messier 37. Veröffentl. Kgl. Sternwarte zu Bonn, N°. 12, 1914.

NORDLUND measures 4 plates and gives the places and magnitudes of 842 stars. The magnitudes are derived from the diameters according to the formula of CHARLIER by means of 214 standard magnitudes that have been determined photometrically by VON ZEIPEL. Many of the bright stars of the cluster are red (colour index $> 0^m.7$), *e.g.* some 50 or 70 % of the stars of the 10th magnitude.

GIEBELER discusses 2 plates taken by KÜSTNER and measured by STROELE. The catalogue contains 1231 objects. The magnitudes have been joined with NORDLUND's scale by comparing those of 450 stars. For the red stars too the photographic magnitude is given.

For our purpose it is a drawback that for the red stars the photographic magnitude is mentioned. This is why the brightest stars, among which many red ones occur, could not be used by us. Excluding these we find from 4 determinations:

$$\pi = 0''.002^5 \pm 0''.0004.$$

Messier 36.

N. G. C. 1960; $\alpha_{1900} = 5^h\,29^m.5$, $\delta_{1900} = +34°\,4'$, $b = +2°$, $l = 142°$; class: $D2$.

Dr. S. OPPENHEIM. Ausmessung des Sternhaufens *G. C.* N°. 1166. Publ. der v. Kuffner'schen Sternwarte in Wien, Bd. III, pag. 271-307, 1894.

Measurements of three photographic plates. The catalogue contains 200 stars. The magnitudes were derived from the diameters, measured in connection with estimates of visual magnitudes found by Dr. PALISA for the greater part of the stars.

The interval of magnitudes is small. We find from 3 determinations:

$$\pi = 0''.005 \pm 0''.001.$$

20 *Vulpeculae.*

N. G. C. 6885; $\alpha_{1900} = 20^h 7^m.6$, $\delta_{1900} = 26°10'$, $b = -5°$, $l = 31°$.

H. Schultz. Micrometrisk bestämning af 104 stjernor inom teleskopiska stjerngruppen 20 Vulpeculae. Kongl. Svenska Vetenskaps-Akademiens Handlingar, Bandet 11, N°. 3, 1873.

The magnitudes have been determined by a photometer in accordance with Argelander's scale.

A. Donner und O. Backlund. Positionen von 140 Sternen des Sternhaufens 20 Vulpeculae nach Ausmessungen photographischer Platten. Bulletin de l'Acad. Imp. des Sciences de St. Pétersbourg, Série V, Volume II, pag. 77-92, 1895.

Measurements of 2 plates taken by Donner at Helsingfors. The magnitudes were taken from Shilow.

M. Shilow. Grössenbestimmung der Sterne im Sternhaufen 20 Vulpeculae. Bulletin etc. ut supra, pp. 243-251.

The magnitudes of the 140 stars, the position of which was determined by Donner and Backlund, were found by measuring the diameters of the images. As standards those 100 magnitudes were used that Schultz had determined already. Shilow uses Charlier's formula $m = x - y \log D - zD$. The probable error of a difference $m - m_{\text{Schultz}}$ is $\pm 0^m.25$.

We have not reduced the magnitudes based on Argelander's scale, to the Harvard scale, because Shilow's magnitudes differ considerably from those of Schultz. We find for the parallax from 7 determinations:

$$\pi = 0''.005 \pm 0''.001.$$

Messier 5.

N. G. C. 5904; $\alpha_{1900} = 15^h 13^m.5$, $\delta_{1900} = +2°27'$, $b = +45°$, $l = 333°$; class: $C3$.

M. Shilow. Positionen von 1041 Sternen des Sternhaufens 5 Messier, aus photographischen Aufnahmen abgeleitet. Bulletin de l'Acad. Imp. des Sciences de St. Pétersbourg, Série V, Vol. VIII, pag. 253-312, 1898.

Measurements of 2 plates, taken resp. by Belopolsky and Kostinsky. The magnitudes have been determined in a rather inaccurate manner, *viz.* by comparing the diameters with the images of stars of 20 Vulpeculae, the magnitudes of which are known.

S. I. Bailey. Variable Stars in the Cluster Messier 5, Annals Harvard Observ., Vol. 78, Part. II, 1917.

Ninety-two stars are dealt with. For 72 the period is mentioned.

Among these 3 have long periods. Moreover the magnitudes are given for 25 comparison-stars.

In SHILOW's catalogue the magnitudes of 1006 stars are mentioned. The interval of magnitudes is small and the magnitudes are inaccurate. Nor did we succeed in reducing them to a more exact scale by means of BAILEY's magnitudes. We find the results $\pi = 0''.0002$ and $\pi = 0''.0009$; consequently as average value:

$$\pi = 0''.0005^6 \pm 0''.0002.$$

According to SHAPLEY the average photogr. magnitude of the variable stars is $15^m.25$ and we found $5 \log. \pi = -16.3$; therefore $M = 15^m.25 - 11^m.3 = 4^m.0$. So we get for the mean absolute magnitude of the variable cluster stars 4.0.

If we determine the parallax from the variable stars with a known period, we find, when making use of HERTZSPRUNG's numbers:

$$\pi = 0''.0002.$$

Messier 13.

N. G. C. 6205; $\alpha_{1900} = 16^h\,38^m.1$, $\delta_{1900} = 36°39'$, $b = +40°$, $l = 26°$; class: $C\,3$.

J. SCHEINER. Der grosze Sternhaufen im Hercules Messier 13, Abhandl. Kgl. Akad. Berlin 1892.

The catalogue contains 823 stars. The magnitudes are uncertain.

H. LUDENDORFF. Der grosze Sternhaufen im Hercules Messier 13. Publ. Astroph. Observ. Potsdam, Bd. XV, N°. 50, 1905.

This catalogue contains 1118 stars. The brightness is not expressed in magnitudes; but the diameters are estimated in 16 "Helligkeitsstufen".

H. SHAPLEY. Studies etc. Second Paper: Thirteen hundred stars in the Hercules Cluster (Messier 13). Contrib. MT. WILSON Observ. N°. 116, 1915.

The photogr. and photovis. magnitudes of 1300 stars have been determined; but of only 650 stars they have been published. For the statistical investigation 1049 magnitudes and colour indices were used.

We make use of LUDENDORFF's catalogue and we availed ourselves of SHAPLEY's results in reducing the "Helligkeitsstufen" to magnitudes. First we can express the "Stufen" in photographic magnitudes by means of a table in SHAPLEY's work (p. 25, Table VIII) and these may be reduced to photovisual ones by means of the Tables XIV and XVI. No correction is wanted for the difference between the scales of HARVARD and MOUNT WILSON, because the visual Harvard

scale is continued only up to $12^m.0$ and for this magnitude agrees with the Mt. Wilson scale.

Now we determine the numbers A_m. For the brightest magnitudes we find then a declivity, which surpasses by far the greatest declivity, found in Kapteyn's curve. This value, great as it is, may perhaps be explained from the manner, in which the diameters have been reduced to magnitudes. Excluding of these values being undesirable *a priori* and not possible on account of the small interval of magnitudes, we have smoothed the numbers observed by a continuous curve. Then we find from 4 determinations:

$$\pi = 0''.00075 \pm 0''.00006.$$

From Shapley's research (l. c. p. 79) we derive for the mean photographic magnitude of the variable cluster stars which are probably δ Cepheids, $m = 15.2$ and we found 5 log. $\pi = -15.4$, so that according to our determination of the parallax their mean absolute magnitude $= 4.8$ [1]).

From 2 variable stars with known period Shapley (l. c. p. 82) found for the parallax the value:

$$\pi = 0''.00008.$$

Messier 67.

N. G. C. 2682; $\alpha_{1900} = 8^h45^m.8$, $\delta_{1900} = +12°11'$, $b = +34°$, $l = 183°$; class: *D* 2.

E. Fagerholm. Ueber den Sternhaufen Messier 67. Inaug. Diss. Upsala, 1906.

The catalogue contains 295 stars. The magnitudes were derived from the diameters by means of Charlier's interpolation-formula, after the visual magnitudes of 15 stars had been determined photometrically.

H. Shapley. Studies etc. III. A catalogue of 311 Stars in Messier 67, Contrib. Mt. Wilson Observ. N°. 117, 1916.

For all stars the photogr. magnitudes have been determined and also the photovisual ones for all stars within 12′ of the centre. In this way 232 colour indices were found. Shapley finds a much greater number of back-ground stars than would be expected.

Olsson's catalogue cannot be used on account of the inaccuracy of the magnitudes.

We first make use of Fagerholm's catalogue. The magnitudes that are expressed in the *P. D.* scale, are reduced to the Harvard scale by adding a correction $-0^m.2$.

[1]) The values of the parallax and the mean absolute magnitude given here, are to be preferred to the preliminary results published in the first communication.

Now we derive from 2 determinations (the interval being only 2 magnitudes):

$$\pi = 0''.001 \pm 0''0007.$$

According to SHAPLEY (l. c. p. 10) the difference FAG.-MT. W. is constant $= + 0^m.24$ and as HARV. = MT. WILSON photovis., we have also: FAG.-HARV. $= + 0^m.24$. We have taken FAG.-HARV. $= + 0^m.2$, so that the magnitudes used should be correct. Upon closer inquiry, however, the difference FAG.-SHAPLEY appears not to be constant, but to vary with the magnitude. We have determined the errors of FAGERHOLM'S scale by comparing the magnitudes of 156 stars, and afterwards we have calculated the numbers A_m for the corrected magnitudes. Now we derive for the parallax from only one determination that can be used:

$$\pi = 0''.002.$$

By telling off SHAPLEY'S catalogue we find for the parallax the values $\pi = 0''.001$ and $\pi = 0''.002$. Summing up, we may assume for the parallax of this cluster:

$$\pi = 0''.002.$$

For this cluster SHAPLEY determined the colour indices of *all* the stars, perceptible on the plate within a circle with a radius of $12'$. But here, too, no great value can be attached to a comparison of the distribution of colours, found by SHAPLEY for every M, with SCHWARZSCHILD'S table. For it is not certain that all stars up to $13^m.0$ are visible on the plate, and just here the separation of cluster stars and back-ground stars offers great difficulties. According to SHAPLEY the distribution of colours, expressed in percentages of the numbers of stars of determined absolute magnitude, is as follows:

Type \ *M*	+ 4.0	+ 3.0
B	0	0
A	0	15
F	38	30
G	51	20
K	11	30
M	0	5

Messier 11.

N. G. C. 6705; $\alpha_{1900} = 18^h\ 45^m.7$, $\delta_{1900} = -6°23'$, $b = -4°$, $l = 355°$; class : *C*3 [1]).

W. STRATONOFF. Amas stellaire de l'écu de Sobieski (Messier 11), Publ. de l'Observ. de Tachkent N°. 1, 1899.

The catalogue contains 861 stars. From the estimates and measurements of diameters the magnitudes have been derived by means of the Southern B. D.

H. SHAPLEY, Studies etc. IV. The galactic cluster Messier 11, Contrib. MT. WILSON Observ. N°. 126, 1916 (A. P. J. Vol. 45, 1917).

For 458 stars the photogr. and photovis. magnitudes have been determined. For statistical research 364 stars were available, after the uncertain magnitudes and the stars upon which the EBERHARD-effect may be of influence had been excluded.

We tell off STRATONOFF's catalogue and we determine the quotients $\frac{A_{m+1}}{A_m}$. It then appears that the magnitudes are too inaccurate and cannot be used.

Now we reduce STRATONOFF's magnitudes to SHAPLEY's scale. In order to do so we compare the magnitudes of 293 stars. The results are given in the table subjoined.

$m_{SHAPLEY}$	Sh—Strat.	Number of comp. stars
10.0	+ 1.53	30
5	1.94	44
11.0	1.68	38
5	1.39	26
12.0	1.45	11
5	1.21	14
13.0	0.91	50
5	0.80	27
14.0	0.70	53

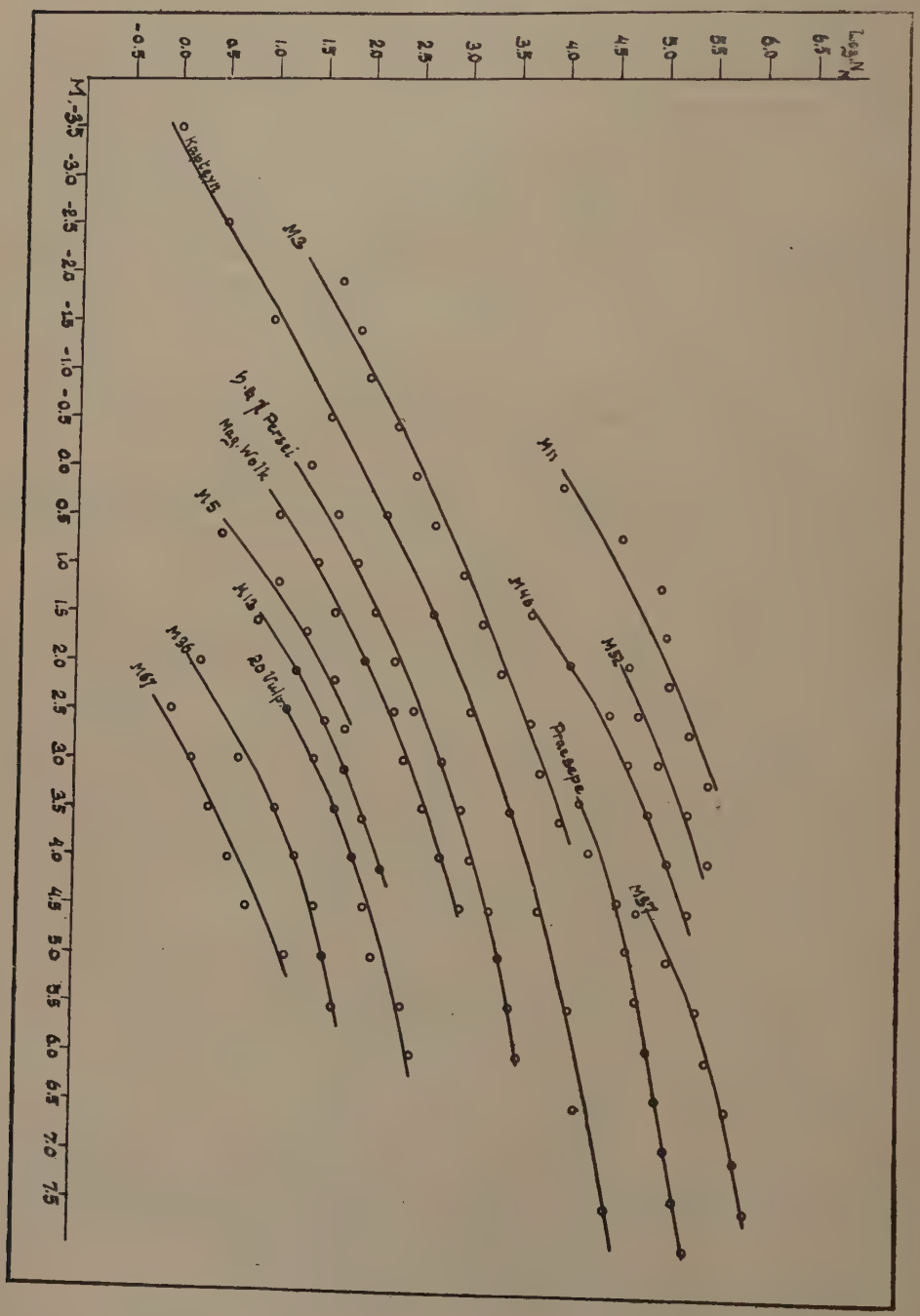
Afterwards we determine by interpolation A_m for the corrected magnitudes. In this way we find for the parallax from 2 determinations:

$$\pi = 0''.00055 \pm 0''.00003$$

[1]) SHAPLEY reckons Messier 11 among the open clusters.

The mean parallax of the globular clusters is 0″.0006 and that of the open clusters (Praesepe excluded) is 0″.003.

The number of parallaxes, determined at present, is still too small to derive conclusions from them as regards the distribution of clusters in space. Perhaps this will be possible, when we shall have extended



our research to more clusters. It will then also be possible to investigate, how far our results give support to the well-known theory of giant and dwarf stars.

From the figure subjoined it is evident that the luminosity curves of the various clusters greatly resemble that found by Prof. KAPTEYN for the stars in the neighbourhood of the sun. And so this method of determining the parallax, proposed by Prof. KAPTEYN, is justified.

In the graphical representation N_M means the number of stars from the brightest star to the absolute magnitude under consideration. As it is only our purpose to compare the relative frequencies of the various absolute magnitudes, we added in each curve a constant amount to log. N_M.

Amsterdam, December 1917.

Physiology. — *"Experiments with Animals on the Nutritive Value of Standard Brown-Bread and White-Bread."* By Prof. C. EIJKMAN and Dr. D. J. HULSHOFF POL.

(Communicated in the meeting of April 26, 1918).

Owing to the scarcity of food the old problem has latterly cropped up again whether, instead of baking white-bread, it would not be more practical to make bread of unboltered meal, since through the process of boltering the grain loses 20—30 % of its nutritive value, according to the degree of milling. The modern technique of grinding enables the miller to separate the flour, which contains the constituents of the endosperm or starchy part, nearly entirely from the bran and the germs of the grain.

The current opinion among people that brown-bread is more nourishing than white, is founded chiefly on the belief that brown bread is more satiating and appeases the appetite for a longer period than white bread does. Though this property must not be underrated, it scarcely needs to be pointed out, that it cannot be an index for the content of nutritious matter. The bran (inclusive of the germs) differs from the flour by a smaller amount of starch and more nutritive salts, fat and protein. However it also contains more cellulose, which is all but indigestible for man, and which also renders it difficult for the alimentary canal to utilize the foodstuffs contained in the bran, since they are for the greater part shut up within thick walls of cellulose. This is why many consider the bran to be useless for man, even noxious, and deem it better that only flour should be baked into bread and the bran should be given to the cattle, which can digest cellulose well and return to us the foodstuffs of the bran in the form of flesh and dairy-products. On the other hand it has been argued that this round-about way via the cow, is also attended with great loss, and that, in striking a balance, it will turn out that man gets more food from wheat in the form of brown bread in spite of less digestibility, than from an equal amount of wheat in white bread.

However, it now appears that the problem requires re-consideration, since it has been proved that, besides the foodstuffs alluded to, the bran also contains peculiar constituents, altogether lacking in flour,

that are highly conducive to the building up of the animal body, nay are even indispensable for its health and growth, viz. the so-called accessory foodstuffs or vitamins.

Here I refer to a paper read by me (E.) some 20 years ago on a fowl's disease (polyneuritis gallinarum) attended with degeneration of the peripheral nerves and motory disturbances arising from a polished-rice diet, and resulting in death within a few days, unless another diet was had recourse to. When the fowl was fed on unpolished rice, or when polishings were added again to the peeled rice, the disease could be prevented, or, if it had already broken out, it could be cured. It appeared namely, that the rice-polishings contained ingredients which, being diffusible, could be readily extracted with water and possessed the same prophylactic and remedial property as the polishings themselves.

The fowl's disease, which can also be produced in other birds (pigeons, rice-birds) in the manner described, shows in many respects a close resemblance to beri-beri, and the researches by VORDERMAN, and many others after him, demonstrated that much of what was brought forward for the one was also applicable to the other.

It must be especially remembered that what has been said regarding rice, also holds for other kinds of grain. Fowls develop the disease, when fed on boltered meal, but not or exceptionally only when given the whole grain or unboltered meal. In keeping with this is the fact that beri-beri does not only manifest itself where polished rice constitutes the staple diet, but is also observed among a population living chiefly on white-bread (LITTLE).

Also in Holland the tropical beri-béri can break out, as has been proved by the cases that lately occurred among native sailors of the Rotterdam Lloyd, described by KOOLEMANS BEYNEN. It is well-known, moreover, that the so-called Ship beri-beri, a comparatively mild form of the disease, which has been seen from time to time especially on Norwegian ships, is also attributed, on reasonable grounds, to too one-sided and too vitamin-poor a nourishment. Nor is it at all improbable that cases of polyneuritis among men, which do occur every now and then, are in some degree allied to beri-beri.

Fortunately the accessory foodstuffs, playing a part here, occur in many other articles of food, such as peas, beans, potatoes, meat, egg-yolk etc. There need be no fear, therefore, for the immediate appearance of beri-beri, at all events not when foods such as white rice and white-bread are not the principal dish. However, if we bear in mind that, as has been seen from what we said about meat, the relative vitamins form a normal constituent of the animal

body, (not evolved in it but derived from the food), it is but natural that, especially in times of scarcity, a vitamin-poor food should be deleterious to the body, even though not causing actual illness.

Comparative experiments on the nutritive value of brown- and white-bread have repeatedly been undertaken, also when vitamins were not thought of. As early as about seven decades back MAGENDIE observed how a dog, fed exclusively on white-bread, lost flesh, got weaker and weaker, and succumbed after 40 days; another dog, fed on bread made from the whole wheat, kept in good health. Similar results were latterly achieved in HOFMEISTER's laboratory with mice. The evidence from such experiments may be disqualified by contending that the laboratory animals actually starve, because they refuse to eat white-bread much sooner than brown-bread. Those nevertheless who believe in animal instinct will not wholly repudiate the significance of this phenomenon.

We preferred to experiment with fowls, first of all because they react most indubitably upon vitamin-poor food with the typical aspect of polyneuritis and do not succumb under equivocal symptoms; and secondly because when the appetite lessens, they readily submit to forced feeding. Forcible feeding is a method also employed in poultry-yards. Intense inanition may in this way be prevented up to the first indication of the disease, viz. atony of the muscle layer of the crop. This causes a more tardy discharge of the crop, so that the ordinary daily allowance cannot be gone through. The typical weakness in the leg-muscles, reminding so forcibly of a similar disturbance attending beri-beri, generally ensues only after some days, sometimes weeks.

Here we also wish to observe that fowls are no more able to digest the cellulose of the bran than man is. The thick walls of the cells of the so-called aleurone-layer, in which chiefly protein and fat are contained, are left intact in their digestive canal. The vitamins, however, as said above, are easily isolated from the bran. The meal, from which the Standard bread was baked, was composed according to the governmental prescription for the white-bread of 60 % inland wheat- and (or) rye-flour, 10 % American flour and 30 % potato-meal; for brown-bread of 70 % unboltered wheat- and (or) rye-meal, 25 % potato-meal and 5 % grits and (or) pollard. Potato-meal is too pure and, therefore, too one-sided a food. The other nutritive constituents of the potato — protein, salts and also vitamins — get lost in the preparation. They putrefy our public waters. It would have been much more reasonable indeed, to eke bread-meal out with powder from dried potatoes, instead of potato-meal. On the

other hand yeast raises the vitamin-content; it has a protective and curative effect with respect to polyneuritis. An accidental advantage is that during the baking the internal temperature of the dough hardly rises above 100° C. As has been shown by GRIJNS for rice and has been corroborated also by myself for other cereals, vitamins are destroyed by moist heat only at much higher temperatures.

In the writer's laboratory two sets of three fowls have been subjected by Dr. HUÏLSHOFF POL to feeding-experiments on brown- and white-bread; they were young, strong animals of about the same age (± 2 years) and weight. The best fed animals were taken for the white-bread experiment; their body-weight averaged ca. 1550 grms; that of the brown-bread fowls was ca. 1400 grms. The bread-ration was ca. 100 grms.

The results of the experiments are given in the graphics. S denotes the moment when forced feeding commenced. P that when the typical symptoms of polyneuritis (disturbances in the gait) made their appearance. For purposes of accurate comparison the changes in the body-weight are not expressed in absolute measure, but in percentages of the initial body-weight.

When first studying the whitebread experiments, we shall notice a fall in the body-weight almost immediately, in spite of normal appetite, which fall continued also after we proceeded to forced feeding. At the close of the 11th week the first fowl (III) developed polyneuritis and succumbed after a few days. A second (II) followed a week later. Henceforth it was fed on brown-bread, just as N°. I, which had lost flesh, indeed, but was not yet actually ill. With this diet the diseased animal recuperated and the fall in body-weight was arrested in either of them.

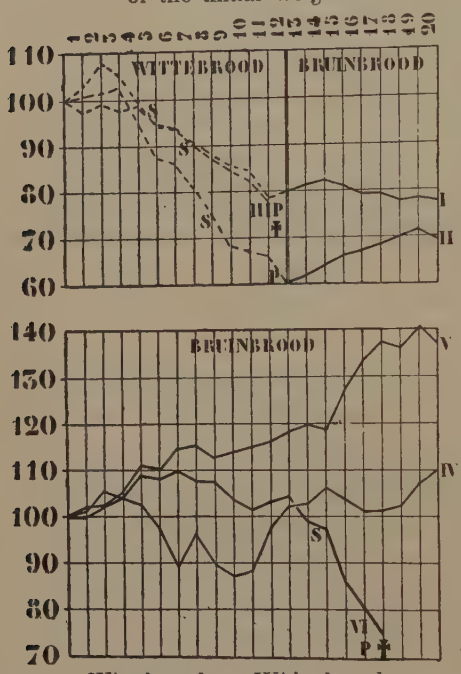
Whereas with a polished-rice diet the fowls develop polyneuritis most often inside of five weeks, not unfrequently even as early as at the end of the 3d week, this outbreak was considerably retarded in the case of fowls on white-bread. It seems probable that this is due to a protective action of the baker's yeast.

Much more favourable were the results of the brown-bread experiments. N°. IV and V remained perfectly healthy and vigorous up to the conclusion of the experiment, which lasted 20 weeks. They increased in body-weight, N°. V even considerably, so that there was no occassion for forced feeding, although a slight inappetence ensued, as is always the case with a uniform diet.

N°. VI fared worse. For the first fortnight it maintained its original weight, but after this time it lost weight constantly; forced

feeding was of no avail. The animal got anaemic, showed the typical aspect of polyneuritis in the 17th week and died a few days later.

Change in body-weight in percentages of the initial weight.



Wittebrood = White-bread.
Bruinbrood = Brown-bread.

Cases in which the same diet is wholesome for the one and injurious to the other animal are not without parallel. Every biologist has to take account of individual differences. These differences also hold for the need of vitamins. GRYNS has even known the disease to break out after a prolonged diet of unpolished rice, though animals that have already been attacked, may most often be cured with the same diet. Attendant circumstances, such as intercurrent diseases, weakening influences may also come into play in such cases. Many even regard an infection as a necessary condition for beri beri to break out.

In resuming it may be allowable. to state that brownbread yields undoubtedly more satisfactory results than whitebread. In connection with what we said at the beginning, we believe the same to hold good also for human nourishment. The drawback of partial indigestibility must not be overestimated. Besides, by improvements in the mode of grinding the miller is able to neutralize this drawback by a finer distribution of the bran along the dry or the wet path, or by removing the coarsest and least nutritive outer layers of the grain. This method should henceforth be more generally applied. Nature, as it were, has destined the bran to eke out the flour; it seems unreasonable, therefore, to separate the two and to replace the bran by potatomeal, which last should be admixed only in the second place and preferably in the form of potato-powder. The use of white-bread should be restricted as much as possible.

Foodstuffs that are fit for man, nay that are preferable for human sustenance, must in times of scarcity not be given to the cattle.

The Hygienic Institute of the Utrecht University.

Physics. — *"An indeterminateness in the interpretation of the entropy as log W"*. By Mrs. T. EHRENFEST-AFANASSJEWA. (Communicated by Prof. J. P. KUENEN).

(Communicated in the meeting of March 23, 1918).

I. A certain quantity of a gas may be given, so large that it may be divided into a great number of portions — great enough for the purpose we are about to discuss — without the usual statistical treatment of the parts losing its value.

Regarding the matter from a thermodynamic point of view we assume:

1. that the entropy of every system strives to attain its maximum.

2. that the entropy of the total mass of gas is equal to the sum of the entropies of the parts.

If in accordance with the kinetic theory, we take the entropy to be the logarithm of the probability of the state of the system, we get the following theses as the analogues of those just given:

1. The state of every system endeavours to approach the greatest probability;

2. The logarithm of the probability of the state of the total mass of gas is equal to the sum of the logarithms of the probability of the states of its parts; or in other words: the probability of the state of the whole is equal to the product of the probability of the states of its parts.

At the same time it may easily be seen that the latter theses are only correct provided the combinations with which we reckon in the determination of the probability of the state of the whole are submitted to certain limitations, which are quite arbitrary *from the combinationary point of view.*

II. We will illustrate this by a simple example, which depends only on the calculus of combinations.

Let us suppose 27 tables, each provided with three holes. In each of the holes a red or a black ball must come to lie. The colour of the ball may be decided by a lottery, in which the chance of drawing a red ball is $^2/_3$, and of a black ball $^1/_3$.

In this case for each table separately — if we still distinguish between the three different holes [1]) — the most probable division of the balls is: two red ones and one black one. For this the probability is [2])

$$\frac{2}{3} \times \frac{2}{3} \times \frac{1}{3} \times \frac{3!}{2!} = \frac{12}{27}.$$

We must now ask: what is the most probable distribution of the combinations over all the 27 tables? We can here still distinguish between the tables. As the most probable distribution we get that in which on only twelve tables two red balls and one black ball lie, on eight of the others three red ones, on six 2 black ones and one red one, and on the last one three black balls. For this distribution the probability is expressed by

$$W_m = \left(\frac{12}{27}\right)^{12} \cdot \left(\frac{8}{27}\right)^{8} \cdot \left(\frac{6}{27}\right)^{6} \cdot \left(\frac{1}{27}\right)^{1} \cdot \frac{27!}{6!\,8!\,12!}.$$

On the other hand, the chance that on each of the 27 tables uniformly two red balls and one black ball should come to lie is given by

$$W_u = \left(\frac{12}{27}\right)^{27}..$$

The ratio between the two is

$$\frac{W_u}{W_m} = \frac{12^{27-12} \,.\, 6!\,8!\,12!}{8^8 \,.\, 6^6 \,.\, 27!},$$

which is very much smaller than 1 [3]).

Let us now suppose the number of balls that can lie on a table, and also the number of tables to be greater; the number of different typical possibilities of division on each table separately (varying from all red to all black) then rises, as also the number of ways in which we can find these types of division spread over the collective tables.

The chance of the most probable division for one particular table becomes *smaller*. The probability W_u, that just this division will be found repeated on every table, becomes therefore represented by a high power of a very small fraction.

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[1]) That is to say, if for a particular combination (e.g. 1 red, 2 black) we count as separate possibilities the cases in which differently coloured balls lie in a given hole.

[2]) The chance of all three being red is $\frac{8}{27}$, of one red and two black $\frac{6}{27}$, of all three black $\frac{1}{27}$.

[3]) For $\frac{6!}{6^6} \cdot \frac{8!}{8^8} \cdot \frac{12!\,12^{27-12}}{27!} = \frac{6!}{6^6} \cdot \frac{8!}{8^8} \cdot \frac{12}{13} \cdot \frac{12}{14} \cdot \ldots \cdot \frac{12}{27}$, in which further $\frac{6!}{6^6} < \frac{1}{64}$, $\frac{8!}{8^8} < \frac{1}{400}$, $\frac{12}{13} < 1$, $\frac{12}{14} < 1$, $\ldots$ $\frac{12}{27} < 1$.

On the other hand, the chance W_m for the realisation of that case, in which the different types are found represented amongst the collective tables in proportion to their probability, will contain a large permutation-factor, and consequently — with a sufficiently large number of tables the ratio W_u/W_m may reach any degree of smallness. It makes a great difference, therefore, — and of course not only to the calculation of the maximum — whether we take the tables collectively as an object of higher order in the calculation of combinations or whether we determine the probability for each table separately and calculate that of the whole as product of the separate probabilities.

III. Suppose that the number of tables and holes for each table are not yet given, but only the total number of hollows in all the tables together, and that it was left to our choice to divide them amongst the tables, then an opinion as to what was the most probable division would be even more arbitrary.

IV. It is obvious, that the above considerations may be applied to the gas, taking into consideration, where necessary, additional conditions.

If we introduce the restriction that in the parts only we attend to all the possible permutations, in defining the most probable division, and that in the system as a whole we do not take into consideration any further permutations between these parts, *only then* does the probability for the state of the whole appear as the product of the probability of the states of the parts.

If on the other hand the total system is regarded as a new object for combinations, an object of a higher order, the probability of the distribution of a special state in the whole is not equal to the product of the probabilities of the parts corresponding to this state. The latter must be corrected by a certain permutation-factor, the magnitude of which is dependent upon the number of the parts, that is either upon the fineness of the division to be chosen at will, or — with a permanently fixed fineness of division — upon the magnitude of the total system.

The question arises: with which $log\ W$ should the entropy be identified?

Only when the said permutation-factor is neglected can it be said that the tending of the parts towards the maximum of their entropy brings with it a striving towards a maximum of the entropy of the whole.

If we adopt the latter view, in other words if we say that the *log W* of a system is *almost the same* as the sum of *log w* of its parts, at the most a sign of inequality is changed into a sign of equality. It is not justifiable, however, *to reverse* the sign of inequality. But this is just what happens when, for instance, the uniform distribution of density in a gas is regarded as the most probable state, and in order to calculate the probability of a distribution slightly deviating from this the relation

$$\log W = \Sigma \log w,$$

is taken as the basis, for in this way each deviating distribution appears as a less probable one [1]).

V. The above analysis is by no means intended to call into question the validity of calculations similar to those indicated in the preceding paragraph, as these rest on the thesis that the entropy of the whole is equal to the sum of the entropies of the parts, a thesis that probably is physically better justified than the combinatory reasonings, at least in the circumstances in which they are applied. The analysis is merely intended to make clear that the *decision of the question whether the probability of the state of a system has reached its maximum or not, depends upon the point of view of the investigator,* and that the *ideas formed from purely combinatory reasonings do not form a satisfactory or conclusive foundation to direct our choice amongst many different standpoints to any one in particular*; further that the choice of our standpoint is made on the ground of various physical intuitions, which are outside the pale of the combination-calculus as such.

That is to say, that the combinational reasonings in question cannot be deduced from a higher principle which may be said to rule nature.

VI. We can show this more particularly in the case of a gas. Let us bring together two cubic centimetres of gas at different temperatures. If it should depend upon the "probability principle" which is to happen, it would be quite indefinite whether an equalisation of temperature would take place or not. It would depend upon the question of which is more important in nature; one cubic centimetre or trillions of cubic centimetres. In the latter case our two cubic centimetres might just be those members of our trillion

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[1]) R. Fürth. *Ueber die Entropie eines realen Gases als Funktion der mittleren räumlichen Temperatur- und Dichteverteilung.* Phys. Zschr. **18**, p. 395—400, 1917.

system, which ought to have different temperatures in order that the whole may get the most probable division of temperature over its parts (trillion tables, and upon each of them million balls). If it is advanced against this that an inequality of this kind must continually appear in precisely the same cubic centimetres, so that *our* two portions of gas may still equalize their temperature, it must not be forgotten that this demands that at the same moment another arbitrary pair of cubic centimetres would be obliged to change temperature in just the opposite direction.

Further it must be remembered that in the case when the subdivision is continued as far as the single molecules we do actually take up the latter standpoint: the momentary kinetic energy accorded to each separate molecule is in itself not the most probable; over a sufficiently large number of molecules, however, the velocities are divided in such a manner that we can only talk of the most probable distribution for the whole of these molecules (quadrillion tables with one ball on each, or, what comes to the same, one table with quadrillion balls).

Zoology. — *"On the primary character of the markings in Lepidopterous pupae"*. By Prof. J. F. VAN BEMMELEN.

(Communicated in the meeting of April 26, 1918.)

On p. 136 of his paper: Zur Zeichnung des Insekten-, im besonderen des Dipteren- und Lepidopterenflügels (Tijdschrift voor Entomologie, vol. LIX, 1915) DE MEYERE raises objections against the comparison of the pupal stage in Lepidoptera with the subimaginal instar of Agnatha; a comparison, which as far as I know, was first made by POULTON [1]), and to which I have expressed my adhesion in my paper on the pupae of Rhopalocera [2]).

He says (translated by me): "It is well known that many investigators believe the pupa to have evolved from a flying imagolike form, the limitation of the wings to the last instar having been acquired later on. In these views I cannot agree with my colleague" (viz. VAN BEMMELEN). "In what way one may imagine the initial evolution of the pupal stage to have taken place, either from a dormant subimago, or from a dormant larva (the latter alternative according to my view being the more probable), in any case I think to be justified in supposing that the Trichoptera, Panorpata, Diptera and Lepidoptera have differentiated out of Neuroptera, after the latter had acquired the Holometabolic metamorphosis they possess to-day. Now the Neuroptera generally have a faintly coloured pupa, which leads a hidden life, concealed in the earth or in a cocoon, and usually has a thin chitinous skin. Such also is the condition with Panorpata, Diptera, and likewise with a number of lower Lepidoptera, as Micropteryx, Lymacodides and many others.

When therefore we meet with special colour-markings exactly in the freeliving pupae of diurnal butterflies, I am inclined to regard this as a wholly secondary feature.... (The italics are mine).

This statement leads me to the following remarks:

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[1]) E. B. POULTON, The external morphology of the Lepidopterous Pupa, its relation to that of other stages and to the origin and history of metamorphosis; Transactions Linnean Society 1890—91.

[2]) J. F. VAN BEMMELEN, Die phylogenetische Bedeutung der Puppenzeichnung bei den Rhopaloceren und ihre Beziehungen zu derjenigen der Raupen und Imagines, Verh. d. Deutschen Zool. Ges. 23 Versamml. 1913.

Against the use of the expression "subimago" in itself, for the pupal stage of Lepidoptera and other Holometabola, DE MEYERE does not seem to have fundamental objections, for as is seen from his own words, he declares that the pupa might be considered as an "inactive subimago," though he himself would prefer the name "inactive larva."

In this preference I cannot agree with him. The conception "larva" implies the presence of provisional organs, as well as the manifestation of a metamorphosis, the moment of which fixes the final point of larval life. Now it is clear, that this point lies at the passage from caterpillar to pupa. Therefore the latter cannot be called an "inactive larva", but only an "inactive subimago". It might even be asserted to represent an "inactive imago", for the provisional larval organs have disappeared, the imaginal organs on the contrary being all present, though still unable to functionate.

But it is especially against the inference, that this subimaginal stage should have been provided with a sufficient mobility to enable it to fly about, after the fashion of the caddisflies when they leave the water, that DE MEYERE raises objection. According to his view, it is much more probable that in none of their phylogenetic stages the Lepidoptera or any of their kin: Panorpata, Diptera, or Neuroptera, were ever on the wing before the very last moult, so before they fully deserved the designation "imago".

Now I must admit, that this supposition of the occurrence of a flying subimaginal instar among the ancestors of these groups of Insects is merely a hypothesis, which can only be supported by arguments of probability, while most assuredly important objections can be opposed against it. One of these difficulties I will indicate myself: Holometabolic Insects may indeed be compared still to other Hemimetabola than precisely the Agnatha, and moreover to Ametabola also, and this comparison may lead to raising the question, if the pupal stage might not best be compared to the last instar but one of these groups, to which belong insects, whose different instars are much more similar to each other than those of Holometabola, because all of them differ less from the imaginal condition, or, what means the same, because they have all deviated in a minor degree from the original Insect-type.

In them we see the wings protrude at an early stage as lateral outgrowths of the dorsal body-wall and increase in size at each following ecdysis, though entering into function at the last one only.

Why should this course of development be less primitive than that of caddisflies? Might not the curious phenomenon, that

the subimaginal instar of the Ephemeridae, after moulting at the surface of the water, flies about for a few moments, then to moult again and immediately afterwards to proceed to copulation, rather be taken as a speciality of the Agnathous life history, without any deeper significance, and therefore of no importance for the explanation of Holometaboly with its dormant pupal stage.

On this point I dare not pronounce a definite opinion, but should like to point out, that in trying to find an answer to the above stated question, we must take into account various general considerations, in the first place that of the development of wings in its totality, viz. the question how Insects (at least Pterygogenea) acquired their wings. For this decides about the question whether we are to suppose that the ancestors of modern Pterygote Insects never passed through a period, in which they moved about on the wing before attaining sexual maturity, or that the beginning of the functional activity of the wings (howsoever acquired) became more and more postponed to the last instar. If we are right in accepting the second alternative, and therefore in believing that the oldest winged insects could already make use of their wings shortly after their birth, the Agnatha may have retained a last trace of this ancient condition. The apparently absurd fact, that these animals fly about in their subimaginal coat for a few moments only, might then be explained by the assumption, that they gradually postponed the start on the wing to later instars, under the ever increasing influence of their secondary adaptation to life in the water. Then the difference between them and other Hemimetabola would not consist in a greater originality of the latter, but in a different mode of deviation from the primitive condition, viz. by the complete removal of the initiation of real flying to the imaginal instar.

The supposition of such a retardation in the transition to flying life-habits is diametrically opposed to the explanation assumed for many other phenomena in metamorphosis, viz. that the manifestation of new characteristics is gradually removed to ever younger instars. In my opinion the former supposition is as well justified as the latter. When for instance Weismann (rightly I think) assumes that changes in colour-markings of certain caterpillars, becoming visible at their last ecdysis only, have been transferred to younger stages in species near akin by a process of precession of development, the opposite course of events may also be considered possible, viz. that a colour-pattern of the wings, which originally came into existence together with the wings themselves, now

only appears a long time after the stage in which the rudiments of the wings first become visible.

Now what is true for the colour-pattern, may as well be applied to the wings themselves.

I do not intend to enter into these considerations more profoundly, as it is irrelevant for the solution of the question, whether or no the colour-pattern on the wing-sheaths of Rhopaloceran pupae possesses phylogenetic significance. On the contrary it seems to me that in this way the question is made unnecessarily intricate. For the difference between the Lepidopterous pupa and the imago emerging from it, as well as between this pupa and the last instar but one in Hemimetabola, only consists in the limited mobility and the temporary suspension of food-supply and excretion in the pupa. In my opinion there can be no doubt that it has lost these functions, and that this loss happened gradually. For we are justified in considering the sculptured and movable pupae of primitive Lepidoptera as more original forms than the mummie-pupae, which are hardly mobile. Why then should not absence of colour and of markings be the consequence of a gradual regression of these characteristics?

Of course this explanation may be as well applied to Neuroptera as to Lepidoptera; DE MEYERE himself concedes that the pupae of Neuroptera "mostly live hidden in the earth or in cocoons, and that their chitinous envelope is thin *and only poorly coloured*". (The italics are mine).

The causes for the regression of existing colour-patterns — viz. darkness and absence of sharpsighted enemies — which obtain all over the animal kingdom — may therefore have exerted their influence on Neuroptera. But this need not involve that the primitive Neuropterous ancestors of recent Lepidoptera already had concealed and immovable pupae. In any case those ancestors had to pass through a long range of thorough transformations, during which especially the youngest larval instars deviated ever more from the original type of the Insect, and in so doing came to differ from the last instar as well as from the last but one.

Those two stages on the contrary remained alike in all important points, though they came to differ from each other in minor accessory characters, which for the pupae chiefly consisted in the loss of mobility, with all its consequences. But apart from this immobilisation it retained the old primordial characters without or with only small modifications, and where a change still occurred, this depended more on katabolic phenomena, e.g. partial or total extinction of colour-markings, than on progressive alterations.

Therefore I think that we need no more ascribe a secondary character to the pupal stage of Lepidoptera, than we should be inclined to do so to the larval or nymphal instar of Hemi-or Ametabola. A grasshopper during the succession of its moults, passes through a series of successive stages of colour-pattern as well as a moth. The idea that the last stage but one of this series bears a different character from the preceding instars or the following ultimate stage, would never occur to us. Neither is this supposition necessary or useful for the understanding of the Lepidopterous design. That the latter is secondarily modified, is beyond doubt, it has been changed in all stages, but precisely in the pupal stage less so than in the preceding larval instar or the succeeding imaginal state, as SCHIERBEEK has shown by comparing the pupal design with that of the caterpillar in its first instar.

As to the colour-pattern of the pupa, the same considerations can be applied to it as to so many of its further properties. POULTON e.g. has pointed out, that in the pupae of those butterflies, whose forewings show a denticulated outer margin, the wing sheaths do not stop at that broken line, yet clearly marked out on its surface, but continue for a short bit and then end in an unbroken front line. He rightly takes this feature as an indication, that the ancestors of those butterflies at one time possessed normally rounded wings. In the same way he was able to show, that in those moths whose females have only vestigial wing-rudiments (the wings of the male sex being well developed) the female pupae differ much less from the male ones, because their wing-sheaths are only a little bit shorter than those of the males.

Likewise the difference between the sheaths for harbouring the filiform antennae of the females and those for the pectinate ones of the males was found to be smaller than that between these antennae themselves.

Would not all these features be caused by a recapitulation of their phylogeny, by the preservation during the subimaginal stage of former conditions which have lost their original meaning.

On this topic DE MEYERE makes the following remark: "It is difficult to explain the presence of this line" (viz. POULTON's mark) "already on the young pupal wing, otherwise than by anticipation of hereditary tendencies. Anyhow a sufficient number of instances can be adduced of cases in which features of different stages are transferred to the pupa in both directions, as well from the imago as from the larva . . . . . To this same influence of precocious entrance into activity might also be ascribed the fact, that certain

markings of the imaginal wing are already visible on the pupa, e.g. the submarginal spots of Vanessidae. Especially when, as VAN BEMMELEN has pointed out, the imaginal wing-pattern, during the beginning of its ontogenetic development, at first shows reminiscences of older more generalised types, we can understand, that the pattern of the wing-sheaths precisely reproduces these stages, without our being obliged to assume that the imago received its colour-markings from the pupa, and that the latter once moved about on wings ornamented in the same style".

Referring to these considerations of DE MEYERE I should like to remark, that I do not in the least suppose the imago to have drawn on the pupa for its colour-pattern, as may clearly be seen from the inferences on p. 358 of my paper: On the phylogenetic significance of the wing-markings of Rhopalocera, (Transact. 2d Entom. Congress, Oxford 1912), in which I point out the facts, that: 1. only the external surface of the wing-sheaths, harbouring the developing primaries, wear colour-markings, in contrast to that of the secondaries hidden beneath it, while of course both pairs of the imaginal wings develop a colour-pattern on both their surfaces; and 2. that the primordial or vanishing pattern on these imaginal wings is still more primitive and therefore phylogenetically older than the colour-pattern on the pupal sheath, so that there is as little reason to suppose that the latter received its pattern from the young imaginal wing hidden in its interior, as to make the opposite supposition.

The transference of imaginal features to younger instars seems probable to me also, as may be seen from the foregoing remarks. When however DE MEYERE calls this transference anticipated entrance into activity, he must have in view the activation of latent hereditary factors, and so must admit the presence of those factors in the genetics of the species. They therefore are connected with former periods of phylogenetic development, or in other words: the colour-pattern of the pupal sheaths must once have ornamented the wings of an insect flying about (or at least walking about) with them. Whether this insect was the imago or the subimago, is a question for itself, but in any case DE MEYERE's expression about "anticipated activation" includes the inference, that he also considers the pupal colour-markings as a recapitulation of a phylogenetically older stage.

Trying to enter into his ideas, I suppose them to have taken the following course: The imaginal instar of Lepidoptera was of old preceded by an uncoloured pupal stage. In the ancestry of the recent butterflies the peculiar habit was acquired, that their pupae no longer lived in

hidden localities, and therefore came in need of protection by mimicking- or by warning-colours. They provided for this need by means of anticipated activation, viz. by transferring the then existing pattern of their forewings to the external surface of the pupal wing-sheaths.

This pattern persisted on the pupa, even after the wings of the imago had acquired the new pattern, such as is found on them to day, by the further modification of the old one.

Even if this view of the course of phylogenetic development should prove right, which I consider rather improbable, it would not diminish in any way the phylogenetic significance of the pupal pattern, and so there would be no need to consider this pattern as wholly secondary and therefore destitute of all importance for the phylogeny of Lepidoptera. For this it would seem, is what DE MEYERE means by his words mentioned in the beginning of this paper: which fully cited run as follows:

"When precisely in the free-living pupae of the butterflies we find special colour-markings, I would consider this as a wholly secondary feature, the body having first acquired certain pigment-spots, to which sympathetic markings of the wingsheaths afterwards were added. That the latter show a certain connection with the veinal system, cannot astonish us, when we take into consideration the special importance of the veins as respiratory and circulatory vessels".

Against this view I wish fully to maintain my own, viz. that the colour-markings of the butterfly-pupae — those on the body as well as those on the wing-sheaths — should be considered as an original pattern, the whole-colour of white, yellow, brown or black pupae of most moths resulting from the loss of this primitive design.

Regarding in particular the harmony between abdomen and wings, in colour-hues as well as in design, we may remark that such a similarity is a generally occurring feature, not only with pupae but even and in a higher degree with imagines. Without doubt this harmony will often root in a secondary modification of shades and markings, of the abdomen as well as the wings, which we may ascribe to sympathetic correlation, but this need not oblige us to doubt that both patterns result from a primitive one, or to abstain from searching after the vestiges of this primitive pattern on both those regions of the body.

What is true for the imagines, is certainly right for the pupae, even in a higher degree; remnants of the original design may be more probably expected on them and be found there in a more complete state, because the imagines are exposed to greater versabi-

lity of life-conditions and external influences, even more so than the caterpillars, their habits of moving about and resting, of nourishing and propagating being more varied.

Both caterpillars and imagines in these respects surpass the nearly immovable and lethargic pupae.

De Meyere's views on this topic seem to be the cause, that while attaching great importance to the differences between the pattern on the pupal wing-sheaths of nearly related forms, such as *Euchloe cardamines*, *Pieris = brassicae*, *Aporia crataegi*, he only pays very slight attention to the facts pointed out by me, viz. the great similarity between the pupal designs in several families of Rhopalocera e. g. Papilionids, Pierids and Nymphalids, a similarity not only far exceeding the resemblance between the wing-patterns of the imagines that emerge from those pupae, but also rooting in the nearer connections of this pupal pattern with the primordial and ephemeric design, which appears on the developing wings during the course of the pupal life, and only gives place to the conclusive imaginal pattern in the very last days before the emergence of the imago.

These vestigial markings on the rudiments of the wings hidden in the pupal sheaths, moreover prove to us that a primordial pattern may easily continue its existence in concealment; therefore such notions as "sympathetic colouration" or "influence of illumination and surroundings" need not be invoked in order to explain the manifestation of such a pattern.

Though the absence of markings may, in all probability, be connected with concealed life-habits and with absence of light, it would not do to consider these influences as the direct and unavoidable causes of the deterioration of the pattern. For the pattern is evidently able also to persist hidden under the pupal sheath, though in some forms it is retained much clearer and more complete than in others, without our being able to find an explanation for this difference.

Now what holds good for the wings inside the pupal sheaths, will probably also apply to those sheaths themselves. Taking this inference for granted, we might expect, that also in some of those Lepidoptera, whose pupae conceal themselves in hidden spots, the original colour pattern, on the body as well as on the wings, might have been more or less preserved.

This turns out to be really the case, as I found when studying the pupae of Chaerocampinae amongst Sphingidae, and of several genera of Geometridae. In contrast with the majority of the genera belonging to these families, whose pupae are black, brown, yellow

or white all over, the genera in question show a well marked and regular design of black markings on a light background. Yet the majority of these pupae certainly live under nearly similar circumstances as those of their relations, i. e. concealed in the earth, in cocoons or between leaves.

It is worth remarking that precisely the Chaerocampinae do not hide in the earth for the object of pupation, as many other Sphingidae do, but remain on the surface and there construct a coarse cocoon of small lumps of earth glued together with threads.

In the same way many Geometridae do not pupate inside the earth, but above it; their tissue often being so loose, that the pupa may be seen inside. I suppose that this may be the cause of the colour-markings on these pupae persisting, whereas those on their near allies have disappeared by obliteration in consequence of total darkness.

Yet the Chaerocampa-pupae in so far undoubtedly show the influence of their concealed habitat, as their markings not only are variable in the highest degree, but also show a marked tendency to obliteration. In this respect they agree with the primordial design on the imaginal wings inside the pupal sheath, and also with the maculated pattern of those butterfly-pupae, in which the original colour-mosaic is replaced by a sympathetic general hue, e.g. the uniformly green pupae of *Pieris napi*, on which the identical spots as on *P. brassicae*, may easily be detected though much smaller and less sharp than on the latter (comp. VAN BEMMELEN, Phylogenetische Bedeutung der Puppen-Zeichnung, and SCHIERBEEK: The significance of the setal pattern in caterpillars and its phylogeny).

Therefore though the colour-design of the Chaerocampa-pupae shows deep traces of obliteration, it nevertheless is clear, that this design is founded on the same groundplan as that of butterflies. In my just-mentioned paper I have proposed a system of names (comp. fig. 6 on p. 115), according to which seven chief ranges of spots might be distinguished, called by me the dorsal, dorsolateral, epistigmal, stigmal, hypostigmal, ventrolateral and ventral rows of spots. In his essay Dr. SCHIERBEEK has pointed out, that the names of W. MÜLLER and WEISMANN, who use the expressions supra- and infrastigmal, have priority.

These rows of spots may all be met again on the pupae of sundry species of *Chaerocampa* as well as on those of *Deilephila* (e. g. *euphorbia* and *elpenor*) in various degrees of clearness and completeness.

No less striking than this correspondence in colour-design between

Sphingidial and Rhopaloceran pupae, is the connection between the markings on the pupae of the Sphinges and on their caterpillars and imagines respectively. Among the material at my disposal I found this similarity most distinctly marked in *Deilephila celerio*, as far as general completeness goes, though for certain details or on special parts of the body, other related forms sometimes showed the similarity still better and more complete, or in a more original form, as I hope to point out in a following communication.

Though I still lacked the occasion to extend my investigations to living caterpillars in their different instars, or to the development of the pupal skin beneath the last larval coat, or the imaginal epidermis inside the pupa, I do not doubt a moment but these transgressive stages will strengthen my conclusions as to the comparability of larval, nymphal and imaginal colour-design, viz. that all three are simply modifications of one and the same ground-plan, which manifests itself clearest in the pupa.

Groningen, April 1918.

Physics. — *"Calculation of some special cases, in* EINSTEIN's *theory of gravitation"*. By Dr. GUNNAR NORDSTRÖM. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of April 26, 1918).

As an application of the theorems deduced in two preceding papers for EINSTEIN's theory [1]) of gravitation, we shall now calculate the gravitation field and the stresses for some special *stationary systems with spherical symmetry.*

First the state at a surface of discontinuity will be investigated.

§ 1. *Introductory formulae.*

In a field with spherical symmetry a surface of discontinuity necessarily is a sphere. This surface will be considered as the limiting case of a layer of finite depth, and we shall only have to pay attention to such surfaces in which in the limit some component of the material stress-energy-tensor increases above every arbitrary limit so that the line-integral across the layer remains finite. In general at such a surface of discontinuity there evidently works a surface-tension P:

$$P = \lim_{r_2 - r_1 = 0} \int_{r_1}^{r_2} \mathfrak{T}_p^p \, dr, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where r_1 denotes the inner radius of the layer, and r_2 the outer one. The radical component of the stress-tensor $\mathfrak{T}_r^r$ on the contrary we shall suppose never to pass every arbitrary limit; in other words we assume that:

$$\lim_{r_2 - r_1 = 0} \int_{r_1}^{r_2} \mathfrak{T}_r^r \, dr = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

First we shall consider a general surface of discontinuity and only afterwards we shall introduce special assumptions. We start from the first and third formulae (38) I and from (39) I. (From these three formulae the second formula (38) I may also be derived, but

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[1]) G. NORDSTRÖM, On the mass of a material system according to the gravitation theory of EINSTEIN. These Proceedings XX, 1917, p. 1076 (cited further on as I) and: On the energy of the gravitation field in EINSTEIN's theory. These Proceedings XX, 1918 p. 1238 (cited further on as II).

we do not need this). The system of coördinates will be fixed by the conditions:

$$v = r, \quad \text{viz.} \quad p = r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Putting further:

$$\mathfrak{T} = \sqrt{-g}\, T = u\, w\, T, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and applying a simple transformation, we can write for the mentioned starting formulae:

$$-\frac{1}{u^2}\left(1 + 2r\frac{w'}{w}\right) + 1 = r^2 \varkappa\, T_r^r\,, \quad . \quad . \quad . \quad . \quad (5)$$

$$\frac{d}{dr}\left\{r\left(1 - \frac{1}{u^2}\right)\right\} = r^2 \varkappa\, T_4^4\,, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$\frac{2}{r}(T_p^p - T_r^r) + \frac{w'}{w}(T_4^4 - T_r^r) = \frac{dT_r^r}{dr} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

These formulae hold for each stationary gravitation field with spherical symmetry; the system of coordinates only is determined by the condition (3). The quantities u and w determine (when $p = 1$) all components $g_{\mu\nu}$ of the fundamental tensor according to the formulae (25) I.

When T_4^4 is given, the equation (6) determines u as a function of r. By integration across a layer which afterwards by a passage to the limit is changed into a surface of discontinuity with radius $r_1 = r_2 = R$ and after division by R we obtain

$$\frac{1}{u_1^2} - \frac{1}{u_2^2} = R\varkappa \lim_{r_2 - r_1 = 0} \int_{r_1}^{r_2} T_4^4\, dr. \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

This formula shows that *u changes discontinuously at a surface of discontinuity where*

$$\lim_{r_2 - r_1 = 0} \int_{r_1}^{r_2} T_r^r\, dr$$

differs from zero. Such a surface which moreover satisfies the condition (2) will be called a *material surface.* The system of coördinates might be chosen in such a way that at the surface u changes continuously, but then p would change discontinuously. In general at least one of the space-components of the fundamental tensor changes discontinuously at a material surface. With the aid of formula (5) we shall now prove, that w on the contrary changes continuously at our material surface, when only the condition (2) is satisfied. Equation (5) gives

$$2\frac{w'}{w} = \frac{u^2}{r}\left(1 - r^2 \varkappa\, T_r^r\right) - \frac{1}{r}, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and by integration across the layer we obtain

$$\log w_2^2 - \log w_1^2 = \int_{r_1}^{r_2} \left\{ \frac{u^2}{r} (1 - r^3 \varkappa T_r^r) - \frac{1}{r} \right\} dr \quad . \quad . \quad . \quad (10)$$

We shall only consider gravitation fields in which u is everywhere finite and when in the limit we pass to an infinitely thin layer the limiting value of the integral on the right-hand side becomes zero according to the assumption (2).

Now we shall apply formula (7) and substitute in it the expression (9) for $\frac{w'}{w}$ and the expression (6) for T_4^4. Multiplying further by $\frac{urdr}{2}$, we find

$$u\,(T_p^p - T_r^r)dr + \tfrac{1}{4}\{u^3(1-r^3\varkappa T_r^r) - u\} \left\{ \frac{1}{\varkappa r^3} \frac{d}{dr} r\left(1 - \frac{1}{u^2}\right) - T_r^r \right\} dr = \frac{ur}{2} \frac{dT_r^r}{dr} dr. \quad (11)$$

This equation must be integrated over a layer and afterwards we must pass to the case of an infinitesimal depth. In order to obtain as a first term on the left-hand side the surface tension P as defined by equation (1) we must moreover multiply by w. We shall however not continue our general investigation, but rather consider two more special cases.

§ 2. *Investigation of the state at a material surface.*

First we investigate the case that at the limit T_4^4 surpasses any value, so that the right-hand side does not become zero, but that $\frac{dT_r^r}{dr}$ remains finite, so that on both sides of the surface of discontinuity T_r^r has the same value.

In (11) we first consider the part of the left-hand side which after integration gives

$$I = \tfrac{1}{4} \int_{r_1}^{r_2} \{u^3 (1 - r^3 \varkappa T_r^r) - u\} \frac{1}{\varkappa r^3} \frac{d}{dr} r\left(1 - \frac{1}{u^2}\right) dr =$$

$$= \frac{1}{4\varkappa} \int \frac{1}{r^3} \{u^3 (1 - r^3 \varkappa T_r^r) - u\}\, d \left\{ r\left(1 - \frac{1}{u^2}\right) \right\}.$$

We have to calculate the value of this expression for the limit $r_2 - r_1 = 0$. In this limiting case r constant $= r_1 = r_2 = R$, so that we have

$$d \left\{ r\left(1 - \frac{1}{u^2}\right) \right\} = 2R \frac{du}{u^3}.$$

We thus obtain

$$\lim_{r_2 - r_1 = 0} I = \frac{1 - R^2 \varkappa T_r^r}{2\varkappa R} \int_{u_1}^{u_2} du - \frac{1}{2\varkappa R} \int_{u_1}^{u_2} \frac{du}{u^2} = \frac{u_2 - u_1}{2\varkappa R} \left(1 - \frac{1}{u_1 u_2} - R^2 \varkappa T_r^r \right).$$

Now we have treated one part of the left-hand side of (11) by integration and by passage to the limit. Of the remaining parts of this left-hand side those containing T_r^r remain zero at the passage to the limit according to our assumption (2), u remaining moreover finite. The part containing T_p^p on the contrary does not become zero. The right-hand side has the value zero at the limit, as we have assumed T_r^r to change continuously at the surface of discontinuity. Multiplying our equation still by w, which quantity we have proved to change continuously at the surface, so that at the limit it may be considered as constant, we obtain:

$$P = - \frac{w}{2\varkappa R} (u_2 - u_1) \left(1 - \frac{1}{u_1 u_2} - R^2 \varkappa T_r^r \right) \quad . \quad . \quad . \quad (12)$$

Together with (8) this formula expresses the laws for a surface of discontinuity of the kind we now consider. These formulae will be applied to the special case that all matter that is present is situated in the material surface. T_r^r being continuous, we have in this case $T_r^r = 0$. Further we have according to (6) both inside and outside the surface

$$r \left(1 - \frac{1}{u^2} \right) = \text{const.} \qquad (r \neq R) \quad . \quad . \quad . \quad . \quad (13)$$

When $r = 0$, u cannot be zero, so that the value of the constant within the surface must be zero. We thus find for $r < R$, $u = 1$ and therefore also

$$u_1 = 1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Within the spherical material surface we thus have a euclidic space. (This is of course true for every hollow sphere; the distribution of mass and stress on the outside only has spherical symmetry). Outside the material surface the constant in equation (13) has not the value zero, but a value, proportional to the mass of the system which is given by formula (15) II:

$$m = \frac{4\pi a}{\varkappa} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15a)$$

We thus have for u_2:

$$u_2 = \frac{1}{\sqrt{1 - \frac{\alpha}{R}}} \quad \ldots \ldots \ldots \quad (15)$$

For w we have at our surface:

$$w = c\sqrt{1 - \frac{\alpha}{R}} = \frac{c}{u_2} \quad \ldots \ldots \ldots \quad (16)$$

This may be proved e. g. by putting $\varepsilon = 0$ in formula (12) II which holds outside our surface. Also by putting $r = R$ we obtain the value (16) at the surface, and formula (9) shows afterwards (as within the surface $u = 1$ and $T'_r{}^r = 0$), that this constant value of w holds also everywhere inside the material surface.

Introducing the expressions u_1, u_2, and w, we find for the surface tension P

$$P = -\frac{c}{2\varkappa R}\left(1 - \sqrt{1 - \frac{\alpha}{R}}\right)^2 \quad \ldots \ldots \quad (17)$$

This formula expresses the relation between the surface-tension, the mass and the radius. Expressed in the usual units the surface-tension is cP (comp. 1 p. 1079). The constant of mass α is also connected with the right-hand side of equation (8). After introduction of the values of u_1 and u_2 this equation gives

$$\alpha = \varkappa R^2 \lim_{r_2 - r_1 = 0} \int_{r_1}^{r_2} T_4^4 \, dr. \quad \ldots \ldots \ldots \quad (18)$$

In the euclidic space inside the material surface we have not the same velocity of light as at an infinite distance from our system, but a smaller velocity

$$c\sqrt{1 - \frac{\alpha}{R}}.$$

We thus have a representation of EINSTEIN's idea on the influence of distant masses on the velocity of light in our part of the world.

Expanding the expression (17) for P in powers of α/R we obtain:

$$P = -\frac{c}{2\varkappa R}\left(\tfrac{1}{4}\frac{\alpha^2}{R^2} + \tfrac{1}{8}\frac{\alpha^3}{R^3} + \ldots\right) \quad \ldots \ldots \quad (17a)$$

NEWTON's theory gives for cP:

$$cP = -\frac{km^2}{16\,\pi\,R^4}, \quad \ldots \ldots \ldots \quad (17b)$$

where k is the NEWTONIAN gravitation constant:

$$k = \frac{c^2\varkappa}{8\pi}.$$

Introducing in (17*b*) the expressions for k and m, we find for P an expression, corresponding to the first term of (17*a*). As to the terms of lower order the theory of EINSTEIN agrees therefore with that of NEWTON.

§. 3. *Second example of a surface of discontinuity.*

Now we shall consider another kind of surface of discontinuity viz. one in which

$$\lim_{r_2-r_1=0} \int_{r_1}^{r_2} T_4^4 \, dr = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

but where T_r^r changes discontinuously. Such a surface of discontinuity we have e. g. when an electric charge is spread over the surface.

Formula (8) shows that in the case in question u changes continuously at the surface:

$$u_2 = u_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

Above we showed already by formula (10) that w changes continuously.

This time too we must multiply formula (11) by w, integrate a layer and pass to the limit of an infinitesimal thickness. As in the last part of the left-hand side all quantities remain finite at the limit, this part gives the limiting value zero. As further u and w change continuously, we obtain

$$P = \frac{R}{2} u w (T_{r_2}^r - T_{r_1}^r),$$

or, introducing the components of the volume-tensor $\mathfrak{T}$

$$P = \frac{R}{2} (\mathfrak{T}_{r_2}^r - \mathfrak{T}_{r_1}^r). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

The meaning of this equation is trivial. It expresses the equilibrium between the surface-tension P at the spherical surface and the normal force perpendicular to that surface, the magnitude of which is $\mathfrak{T}_{r_2}^r - \mathfrak{T}_{r_1}^r$, per unit of surface. The gravitation has evidently no influence.

When on the surface we have an electric charge e and inside the surface no matter, we find (II, note p. 1240)

$$\mathfrak{T}_{r_1}^r = 0, \qquad \mathfrak{T}_{r_2}^r = \frac{u w e^2}{8\pi R^4}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

Now we shall assume that neither outside the surface there is any matter except the electric field, and we shall calculate the mass

of the electric sphere. As was proved in II § 1 we have outside the sphere

$$u\,w = c \qquad (r > R), \quad \ldots\ldots\ldots \quad (23)$$

$$T_r^r = T_4^4 = \frac{e^2}{8\pi\, r^4} \qquad (r > R) \quad \ldots\ldots\ldots \quad (24)$$

As inside the sphere and at its surface $u = 1$, we find from (6) by integration up to an upper limit $r > R$

$$r\left(1 - \frac{1}{u^2}\right) = \varkappa \int_R^r r^2\, T_4^4\, dr = -\frac{\varkappa e^2}{8\pi\, r} + \frac{\varkappa e^2}{8\pi\, R} \qquad (r > R),$$

$$\frac{1}{u^2} = 1 - \frac{\varkappa e^2}{8\pi\, Rr} + \frac{\varkappa e^2}{8\pi\, r^2} \quad \ldots\ldots\ldots \quad (25)$$

A comparison with equation (11) II shows, that we must have:

$$a = \frac{\varkappa e^2}{8\pi\, R},$$

and (15a) gives for the mass m

$$m = \frac{e^2}{2R} \quad \ldots\ldots\ldots \quad (26)$$

The charge e being expressed in electro-magnetic units (see II p. 1202) this expression for m is equal to the electro-static energy divided by c^2. Besides the electro-static energy no energy occurs in our system. That outside the electric body no gravitation energy, is present has been proved already in II § 2. The last result says therefore that neither in the electric surface any gravitation energy is accumulated.

§ 4. *A sphere of an incompressible fluid.*

This problem has been treated already by SCHWARZSCHILD, [1]) but as the formulae (5), (6), and (7) lead us by another way quickly to the same result, it may be allowed to develop these calculations as shortly as possible.

That the medium is incompressible means that when at rest

$$T_4^4 = \varrho \quad \ldots\ldots\ldots \quad (27)$$

is a constant characteristic for the medium. The fluid character of the medium demands further that no tangential stresses can occur, so that we have

$$T_r^r = T_p^p = -p, \quad \ldots\ldots\ldots \quad (28)$$

[1]) K. SCHWARZSCHILD, Ueber das Gravitationsfeld einer Kugel aus inkompressibeler Flüssigkeit nach der Einsteinschen Theorie Berl. Ber. 1916 p. 424.

where the pressure scalar p [1]) meanwhile is a function of the place viz. of r. The radius R of the sphere and the mass m and ϱ are related by an equation which is found by integrating (6) from $r = 0$ to $r = R$. As for $r = 0$ u is not zero, while for $r = R$ it has the value $\frac{1}{\sqrt{1 - \frac{a}{R}}}$ (see II equation (11)), we find

$$a = \frac{\varkappa \varrho}{3} R^3$$

and therefore

$$m = \varrho \tfrac{4}{3} \pi R^3 \quad \ldots \ldots \ldots \quad (29)$$

This shows that ϱ plays the part of density.

Integrated from $r = 0$ to an arbitrary upper limit $r < R$ (6) gives further u as a function of r. We obtain:

$$r\left(1 - \frac{1}{u^2}\right) = \frac{\varkappa \varrho}{3} r^3,$$

$$u^2 = \frac{1}{1 - \frac{\varkappa \varrho}{3} r^2} \quad \ldots \ldots \ldots \quad (30)$$

Now w and p have still to be determined as functions of r. The quantities w and p are connected by equation (7). This gives

$$\frac{w'}{w}(\varrho + p) = -\frac{dp}{dr}, \quad \ldots \ldots \ldots \quad (31)$$

so that

$$\frac{dw}{w}(\varrho + p) = -dp.$$

This must be integrated. The integration constant is determined by the fact that at the spherical surface $p = 0$ and $w = c\sqrt{1 - \frac{a}{R}} = c\sqrt{1 - \frac{\varkappa \varrho}{3} R^2}$ (see II equation (12)). We thus obtain the asked connection between w and p:

$$w(\varrho + p) = \varrho c \sqrt{1 - \frac{\varkappa \varrho}{3} R^2} \quad \ldots \ldots \quad (32)$$

Now p will be calculated as a function of r. Introducing in (5) the expression (30) for u and simplifying the equation we obtain

$$2\frac{w'}{w}\left(1 - \frac{\varkappa \varrho}{3} r^2\right) = \frac{\varkappa}{3} r(\varrho + 3p) \quad \ldots \ldots \quad (33)$$

---

[1]) We need not be afraid that this p will be confused with the quantity p which in § 1 has been put equal to 1.

We eliminate $\frac{w'}{w}$ between this equation and (31). In this way we find

$$\frac{2\,dp}{(\varrho+3p)(\varrho+p)}+\frac{\varkappa}{3}\frac{r\,dr}{1-\frac{\varkappa\varrho}{3}r^2}=0 \quad . \quad . \quad . \quad . \quad (34)$$

The integration gives

$$log\frac{\varrho+3p}{\varrho+p}-log\sqrt{1-\frac{\varkappa\varrho}{3}r^2}=const.$$

The integration constant has to be determined with the aid of the condition that for $r=R$ $p=0$. We therefore find

$$\frac{\varrho+3p}{\varrho+p}=\sqrt{\frac{1-\frac{\varkappa\varrho}{3}r^2}{1-\frac{\varkappa\varrho}{3}R^2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

Thus the pressure-scalar p is determined as a function of r.

Eliminating p between this equation and (32) we obtain for w as a function of r the expression:

$$w=\frac{c}{2}\left(3\sqrt{1-\frac{\varkappa\varrho}{3}R^2}-\sqrt{1-\frac{\varkappa\varrho}{3}r^2}\right). \quad . \quad . \quad (36)$$

In this way we have perfectly determined the gravitation field and the pressure distribution inside our sphere. The formulae we obtained become identical with those of SCHWARZSCHILD when for r we substitute

$$r=\sqrt{\frac{3}{\varkappa\varrho}}\sin\chi.$$

§ 5. *On the gravitation field as it may be imagined to exist in the inside of an atom.*

In the theory of atomic structure of RUTHERFORD-BOHR we meet with difficulties arising from the assumption that in an atomic nucleus of very small dimensions there exist units of charge which — at least when they are liberated in the form of electrons — have a greater diameter than the atomic nucleus. As now EINSTEIN's gravitation theory states that the space in a gravitation field when expressed in natural units is non-euclidic, the question arises whether this theory leaves the possibility of the assumption that the atomic nucleus fills a greater space with a narrow neck or perhaps a space which crosses itself at a certain point. This question will be investigated here.

We consider again a stationary system with spherical symmetry. In the same way as above we may define the distance r from the centre of symmetry by putting $p = 1$ viz. by demanding that the periphery of a circle with its centre at the centre of symmetry is $2\pi r$, when expressed in natural units. If we do so in the case in question, the state in the field is not a single-valued but within a certain interval at least a more-valued function of r. It is therefore useful to introduce a new radial space-coordinate of which the quantities in the field are single-valued functions. As such a coordinate the distance s from the centre of symmetry expressed in natural units suggests itself. In order to specialize our discussion we can prescribe a relation between the radius defined by the condition $p = 1$ and s and investigate afterwards whether this is in agreement with a possible distribution of the components T_μ^ν of the stress-energy-tensor.

As a trial we put

$$r = \pm s\left(\frac{s^2}{3a^2} - 1\right), \quad \ldots\ldots\ldots \quad (37)$$

where a is a constant, and we choose the sign thus that a positive value of r corresponds to a positive value of s. For small values of s r and s are proportional and the three-dimensional space is dilated when we come farther away from the centre (viz. from the point $s = 0$). For $s = a$ r reaches however a maximum and when s increases still further the space is contracted and crosses itself at a point in the neighbourhood of $s = \sqrt{3}\,a$. For still higher values of s the space is again dilated.

Before proceeding we still remark that in fact the sign of r does not play a role. Inversing the sign of r in our fundamental formulae (5), (6) and (7) and interchanging also the signs of dr and w' we find from the formulae the same values as above for all remaining quantities. For this reason we take in (37) everywhere the $+$ sign, so that r is taken negative in the interval $0 < s < \sqrt{3}\,a$.

While the following discussions will be based on the fundamental equations (5), (6), (7), we suppose u, w, r, T_r^r, T_p^p, T_4^4 to be functions of s. As s is the distance from the centre of symmetry expressed in natural units we obtain, attending to the meaning of the quantity u (see I § 3)

$$ds = u\,dr, \quad \ldots\ldots\ldots \quad (38)$$

As (37) gives by differentiation

$$dr = \left(\frac{s^2}{a^2} - 1\right) ds. \quad \ldots\ldots\ldots \quad (39)$$

we find for u

$$u = \frac{1}{\frac{s^2}{a^2} - 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

That u is negative for $s < a$, does not cause any trouble, as the fundamental tensor depends on u^2 only.

Now we must introduce in equation (6) the expressions (37) and (40) for r and u. Introducing to begin with the expressions on the left hand-side only we obtain

$$-\frac{s^2}{a^2}\left(\frac{7}{3}\frac{s^2}{a^2} - 6\right) = r^2 \varkappa T_4^4 \quad . \quad . \quad . \quad . \quad . \quad (41a)$$

Introducing the expressions on the right-hand side too we find for T_4^4 as a function of s

$$\varkappa T_4^4 = \frac{6 - \frac{7}{3}\frac{s^2}{a^2}}{a^2\left(\frac{s^2}{3a^2} - 1\right)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

The formulae derived here hold evidently only inside the material system of which the outer boundary may be indicated by $s = S$. In order that the space occupied by the system may cross itself at any point we must have because of (37).

$$S > \sqrt{3}\, a.$$

In the limiting surface $s = S$ we have according to (40) $u < 1$. In order that in that surface u may pass continuously into the value it has in the field on the outside, u must also in the outer field be smaller than 1 for $s = S$. This follows also from formula (11) II, when the system has only a sufficient great electric charge. Further it does not matter that u would change discontinuously at the boundary, if only this is a material plane as considered in § 2.

Formula (41) shows that in the interval $\sqrt{\frac{18}{7}}\, a < s < S$ T_4^4 is negative, which though somewhat startling is not at all absurd. Further formula (41) indicates that T_4^4 becomes infinite for $s = \sqrt{3}\, a$. Within a finite extension there is however only a finite mass of matter, which follows from the fact that $r^2 T_4^4$ is everywhere finite according to (41).

The equations (40) and (41) for u and T_4^4 involve together with (37) that the fundamental equation (6) is satisfied. Now we must still determine w, T_r^r and T_p^p as functions of s, so that also the equations (5) and (7) are satisfied. As (5), (6) and (7) form the complete set of field equations for a stationary gravitation field, we

may choose for one of the quantities w, T_r^r and T_p^p an arbitrary single-valued function of s. When also the expressions for r, u and T_4^4 are introduced, the equations (5) and (7) determine now the two quantities. All these possible material systems give — if only the distribution of T_4^4 is the same — a three-dimensional space of the same curvature, because the formulae (25)I perfectly determine the space-components of the fundamental tensor (when $p = 1$). The curvature of the four-dimensional space-time continuum on the contrary depends also on the distribution of T_r^r which quantity according to (5) influences w. The following simple assumptions might e. g. be made to obtain a definite system : $w =$ constant, $T_r^r = 0$ or $T_r^r = T_p^p$ (normal pressure in all directions). Performing the integration of (15) and (7), we might choose the integration constants in such a way, that at the boundary $s = S$ w takes the value that holds there for the outer field, for, as was proved in § 1, w changes continuously into a surface of discontinuity.

The purpose of our investigation being reached no further calculations will be added. We have shown that EINSTEIN's theory of gravitation really admits such a distribution of the stress-energy-tensor T, that the (three-dimensional) space crosses itself at a certain point. We can also prove without difficulty, that systems can exist in which the space filled with the matter runs out into a narrow neck.

It is still of some importance to investigate the action of the electric forces within the space which is just dilated and afterwards again contracted. We might e. g. investigate the state, when, with constant T_4^4, T_r^r, T_p^p for the non electro-magnetic matter, a point charge was placed at the centre of symmetry. The gravitation field will evidently change. We have not only to calculate this field, but also the laws of the equilibrium and the motion of other electric (point)-changes in the new electric field. Here we must treat the matter as perfectly permeable. These indications may however suffice, which show already that EINSTEIN's theory opens wide possibilities to explain the state in the inside of an atom.

Chemistry. — *"Determination of the Configuration of cis-trans isomeric substances"*. By Prof. J. BÖESEKEN and CHR. VAN LOON.

(Communicated in the meeting of May 25, 1918).

1. The appearance in a number of isomers of unsaturated and cyclic compounds, has undoubtedly been a momentous incitement to the acceptance of VAN 'T HOFF's hypothesis on the carbon atom, which is supposed to lie in the centre of its valencies.

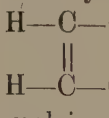
The permanence of the optical activity at moderate temperatures necessitated the attribution of a rather great stability to these valencies. Obviously in cyclic molecules the same rigidity had to be accepted, and also around the double bond.

Apart from objections that may rise against the substance of this supposition — objections connected with hypotheses on the internal structure of the atom — it must be granted that a very elegant interpretation has been given of the existence of the aforesaid isomers.

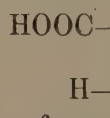
In fact, only very seldom cis-trans isomerism could not be observed when it was to be expected according to this theory, while on the other hand, if identical radicles are united to one of the unsaturated atoms or members of the ring, and therefore no isomers are to be anticipated, they were indeed not to be found.

2. This interpretation of the existence of cis-trans isomers is little to be doubted; however, it is much more difficult to determine which isomer has the cis- and which the trans-configuration.

By a happy coincidence the classical case of cis-trans isomerism, *viz.* that of maleic and fumaric acid, has offered, also in this respect, the greatest certainty.



maleic acid



fumaric acid

The cause is evident: the configuration determination here is based almost exclusively on properties that may be deduced from the molecules themselves.

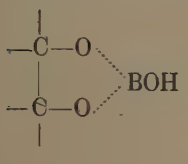
The determination namely of the configuration of geometrical isomers takes place along different lines.

First of all the configuration may be deduced from properties that are to be anticipated in consequence of the reciprocal influence of the groups in the molecule; this is the surest way, if enough (critically examined) data for comparison be available.

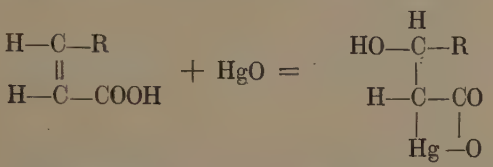
Among these properties are: dissociation constants of acids, formation of anhydride, resolution into optical antipodes, *etc.*

The formation of complex compounds is to be included in so far as the valencies, which are the bearers of cis-trans isomerism, are not attacked.

This is seldom easily established, since the structure of complex compounds is uncertain. Probably we are authorized to use this method in judging the cis-trans isomerism of cyclic glycols by the influence on the conductivity of boric acid, because the boric acid-radicle is united to the oxygen atoms and not to the carbon atoms, which determine the isomerism.



It is doubtful if it may be applied to cis-trans non-saturated acids; if the formation of complex metallic compounds must be represented by the following formula:



or anyhow, if it is to be supposed that the double bond is attacked, we can rely upon this method as little as on all others, by which the bearers of the isomerism are affected (see below).

Now the contrast between the two groupings H and COOH, which are bound to the very simple skeleton of maleic and fumaric acid, is exceptional; besides, the two carboxyl groups may enhance each other's acidity or react with one another under anhydride formation. Also a mutual repulsion of the COOH groups is to be anticipated, from which could be deduced that fumaric acid is more stable than maleic acid.

The particularly simple structure of these acids, by which the carboxyl groups take the leading position, has rendered the above-mentioned considerations so successful in determining the configurations.

As soon as this reciprocal influence fails or the structure becomes much less simple, we have no longer any certainty.

We will examine α- and *iso*-crotonic acid in this respect:

1. The dissociation constants are: α-crotonic acid $2 . 10^{-5}$.
iso- ,, ,, $3{,}6 . 10^{-5}$.

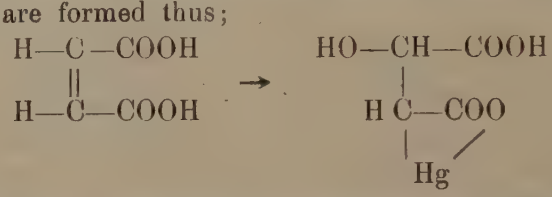
By comparing propionic with acetic acid it could be deduced that a methyl group weakens the acidity, so that in α-crotonic acid the methyl group must lie on the same side as the acid group; in fact acrylic acid ($k = 5{,}6 . 10^{-5}$) is dissociated in a higher degree than

both crotonic acids, and dimethyl-acrylic acid ($\pm 7 . 10^{-6}$, according to preliminary determinations of Mr. P. E. VERKADE, Dissertation Delft 1915, 2nd Note, p. 66) is weaker still. Also citraconic acid is much weaker than maleic acid.

Still one ought to be cautious, for *iso*-butyric acid is somewhat stronger than propionic acid (1.44 to $1,31 . 10^{-5}$) and the dimethyl succinic acids are much stronger than succinic acid (1,9 and 1,3 to $0,6 . 10^{-4}$).

2. Formation of an anhydride is not possible and therefore cannot help us.

3. Formation of complex compounds: BIILMANN has shown that maleic, citraconic and *allo*-cinnamic acid form salts with mercuric acetate, which are soluble in sodium hydroxide, and from which the original acids could not be regenerated by elimination of mercury; in this case β-hydroxy-acids were formed and in consequence B. surmises that the salts were complex mercury salts of these hydroxy-acids, which are formed thus;



In the same way α-crotonic acid remained in solution in the form of a complex mercury salt, which could be precipitated with alcohol. From this salt β-hydroxy-butyric acid was obtained; in consequence one deduces from this too the cis-configuration for ordinary crotonic acid with the higher melting point.

In order to corroborate this result we have subjected *iso*-crotonic acid to the same operation and obtained an insoluble basic mercury salt, which, after decomposition by means of H_2S furnished a mixture of *iso*- and α-crotonic acid.

It may be mentioned in passing, that α-crotonic acid must have been formed *during the elimination of mercury*, for this acid — so far as it originally was present in the *iso*-crotonic acid — was kept in solution as a complex salt and because H_2S does not, or at least extremely slowly, change free *iso*-crotonic acid into α-crotonic acid.

The coincidence of the conclusions from the dissociation constants and from the researches of BIILMANN gives some certainty to the configuration of the crotonic acids. It follows that the formula of these complex compounds is probably different from the one that has been proposed by BIILMANN. However, this method of discernment is valid exclusively for $\alpha\beta$-non-saturated acids; other ethylene derivatives, among which are the esters of isomeric acids, cannot be

distinguished in this way, because they all seem to form complex compounds with basic mercury salts[1]).

From the dissociation constants of *angelic* and *tiglic acid* we can at the very best suspect that in the first acid a hydrogen atom is situated on the side of the COOH group, in the other one of the methyl groups.

The configurations adopted here are supported by the consideration that the most stable acid will be the one in which the relatively positive group is situated as near as possible to the COOH group.

—COOH	HOOC—C—H ‖ H—C—COOH	CH_3-C-H ‖ H—C—COOH	H—C—CH_3 ‖ H—C—COOH	CH_3-C-H ‖ $CH_3-C-COOH$	H—C—CH_3 ‖ $CH_3-C-COOH$
—COOH	fumaric acid	*iso* crotonic acid	α-crotonic acid	angelic acid	tiglic acid
eic acid	no anhydride	—	—	—	—
anhydride	9.3×10^{-4}	$3{,}6\times10^{-5}$	2.0×10^{-5}	5×10^{-5}	1×10^{-5}
$.2\times10^{-2}$	0	0	+	—	—
ex Hg. salt +	stable		stable		stable

About oleic and elaidic acid there is utter uncertainty, because the dissociation constants are not known; it can only be suspected that in the more stable elaidic acid the relatively positive carbon chain is likely to lie on the side of the carboxyl group.

With cyclic cis-trans isomers the importance of cis-trans situated radicles in relation to the ring becomes less as the last widens. [The conception of VON BAEYER that the angle between the directions of the affinities of trans-situated radicles decreases as the ring widens, is not incorrect; only VON BAEYER deduces this decrease from sterical considerations and then it cannot be so very important]; this consideration lessens the certainty of our conclusions about the configuration still more. But now here we meet with the very happy circumstance, that the trans-compounds frequently are asymmetrical and therefore can be resolved into optical antipodes.

If this argument is annulled, as in the case of the hexahydroterephtalic acids, which are both symmetrical, or if a resolution into optical antipodes has not been tried, there is no certainty at all. This may be backed by the following table: (See following page).

We see that the formation of anhydrides, the most important argument with maleic acid, has all but lost its significance in the case of the cyclohexane derivatives, as both 1-2-dicarboxylic acids and neither of the 1-4-acids form an anhydride.

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[1]) B. **33** 1340, 1641, 2692, (1900); **34** 1385, 2906 (1901); **35** 2571 (1902); **43** 568 (1910).

		k	Anhydride	Resolvable
cis-cyclopropane-dicarboxylic acid	1.2	4×10^{-4}	+	—
trans „ „	1.2	2.1×10^{-4}	—	+
cis-cyclobutane-dicarboxylic acid	1.2	6.6×10^{-5}	+	not investigated
trans „ „	1.2	2.8×10^{-5}	—	
cis-cyclopentane-dicarboxylic acid	1.2	1.58×10^{-5}	+	"
trans „ „	1.2	1.2×10^{-5}	—	
cis „ „	1.3	5.4×10^{-5}	+	"
trans „ „	1.3	5.0×10^{-5}	—	
cis-cyclohexane-dicarboxylic acid	1.2	4.4×10^{-5}	+	
trans „ „	1.2	6.2×10^{-5}	+	+
cis „ „	1.3	not determined	+	not investigated
trans „ „	1.3		—	
? cis „ „	1.4	3×10^{-5}	—	symmetrical
? trans „ „	1.4	4.6×10^{-5}	—	

This is the more true of the dissociation constants, whereof the differences in the case of the cyclopentane-dicarboxylic acids are small already, but leastways such that from the acid with the greater constant an anhydride is known.

About the cyclohexane-dicarboxylic acids in this respect we grope in the dark. The 1-2-acid, which has been resolved into optical antipodes and accordingly is undoubtedly the trans acid, is stronger than the cis acid; both acids easily form an anhydride. If in this case it should have been unknown which acid is resolvable, we should probably have come to a wrong conclusion.

With the 1-4-dicarboxylic acids, the classical case of cyclic cis-trans isomerism, *there is no certainty at all*; the one with the highest melting point, which VON BAEYER has denominated trans, has the highest dissociation constant and therefore one should perhaps call it the cis acid. As it as little forms an anhydride as the isomer and neither can be resolved into optical antipodes, the only remaining argument in favour of the current conception is the greater stability; an argument that should be termed weak, considering the slight solubility and the high melting point.

Still the case is not entirely hopeless; after having discussed the

chemical methods that can serve to determine the configuration, we will demonstrate that here too there is a way out.

It is evident that, if less characteristic radicles are bound to the nucleus, as in the cyclohexanediols 1-4 or the hexahydro-toluilic acids, with which no discernment by resolution into optical antipodes is feasible, it seems impossible to determine the configuration.

Here the difference which appears in the formation of complex compounds, for instance of the diols with boric acid, has proved promising; this has been evidenced by the configuration determination of some sugars, but on that point we will not expatiate here.

3. Secondly the configuration may be deduced from what happens if the double bond is saturated; the so formed compounds are different as they originate from the cis or from the trans isomer.

The configuration may also be inferred from the way of formation, either from saturated compounds by elimination of parts of the molecule, or from acetylene derivatives by partial saturation, or by substitution of groups in compounds, of which the configuration is known.

The last mentioned modes of determination, by which the bonds between the atoms are vigorously attacked, have often caused confusion, by which their trustworthiness has been impaired. When applied to fumaric and maleic acid, they at first seemed to answer excellently; we can still assert with satisfaction that fumaric acid is changed by $KMnO_4$ into racemic acid and maleic acid into *meso*-tartaric acid.

Only, the brilliant researches of WISLICENUS about the bromination of both acids, followed by elimination of one molecule of HBr, by which fumaric acid furnishes first racemic dibromo-succinic acid and then bromo-maleic acid, and maleic acid first meso (*iso*-)dibromo-succinic acid and then bromo-fumaric acid, have turned out to be correct only as far as the final products are concerned.

MCKENZIE [1]) and BROR HOLMBERG [2]) namely have demonstrated that *iso*-dibromo-succinic acid with the lower m. p. can be resolved into optical antipodes and this entirely overthrows the deduction.

As well at the addition of bromine to both acids, as at the elimination of HBr, exactly the reverse occurs from what we could expect, and this inversion appears to be rather common.

By the action of PCl_5 on aceto-acetic acid two isomeric β-chloro-

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[1]) Proc. Chem. Soc. **1911**, 150.

[2]) Journ. pr. ch. **84** 145 (1911).

crotonic acids are formed, one of which is volatile with steam. This one has a dissociation constant $= 9{,}5 \cdot 10^{-5}$; the other acid has $k = 14{,}4 \cdot 10^{-5}$. From this it may be concluded with some certainty, that in the first mentioned acid the chlorine atom lies farther from the COOH group than in the other. Now the relatively weaker acid on reduction furnishes the relatively stronger *iso*-crotonic acid; on the other hand the relatively stronger β-chloro-crotonic acid gives rise to the relatively weaker α-crotonic acid; in both cases an inversion must have occurred and we come to the conclusion, as well as in the series maleic acid $\rightarrow$ *iso*-dibromo-succinic acid $\rightarrow$ bromo-fumaric acid, that an inversion has taken place at the attack of the valency, which governs the configuration.

By catalytic hydrogenation only of phenylpropiolic acid in the presence of colloidal platinum 80 % of the theoretically possible amount of *allo*-cinnamic acid was formed; on the other hand, by the action of zinc dust and acetic acid, resp. alcohol, ordinary cinnamic acid was almost exclusively obtained [1]). As the *catalytic* hydrogenation of acetylene compounds appeared to warrant some certainty, we applied it to tetrolic acid, which ought to give chiefly α-crotonic acid.

However during a microchemical investigation, which was executed some years ago with the collaboration of Miss O. B. VAN DER WEIDE, α-crotonic acid could not be found among the reduction products of the sodium salt of tetrolic acid.

By hydrogenation of the free acid under the influence of palladium-sol, crotonic and *iso*-crotonic acid are formed in the proportion of 2 : 1.

We see, therefore, that no more than with the reduction of phenylpropiolic acid, this chemical method is capable of giving us sufficient certainty about the configuration.

4. To cyclic cis-trans diols also this unsafe mode of determining the configuration is generally not applicable, because the correspondent saturated diols cannot be obtained.

The hydro-aromatic glycols form an exception, as they can be obtained from aromatic diphenols, which may be considered as cis diols. Of course this case is not quite to be compared to the hydrogenation of acetylene compounds; it is known with rather great certainty that the OH groups of the phenols are situated in the plane of the benzene nucleus; on the other hand it is to be supposed, considering

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[1]) HOLLEMAN and ARONSTEIN B. **22** 1181 (1889); LIEBERMANN and TRUCHSÄSS B. **42** 4674 (1909); E. FISCHER, Ann. **386** 385 (1912).

the number of isomers, that in acetylene derivatives the substituents lie in a line with the carbon atoms of the acetylene skeleton.

The researches in this field, *viz.* the catalytic hydrogenation of diphenols with the aid of nickel, show, that a *mixture* of the cyclohexanediols is formed; a reduction under the influence of platinum or palladium at a low temperature apparently has not been executed yet.

Now there are general syntheses of these diols, *viz.* from the nonsaturated cyclic hydrocarbons, either by direct oxidation by $KMnO_4$ or *via* the oxides; we have made use of them to prepare the hydrindenediols. According to current ideas the cis diol should be formed exclusively by this reaction[1]):

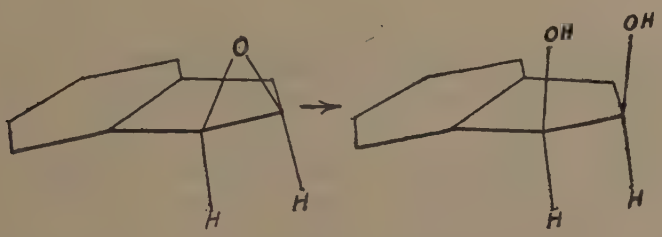


Fig. 1.

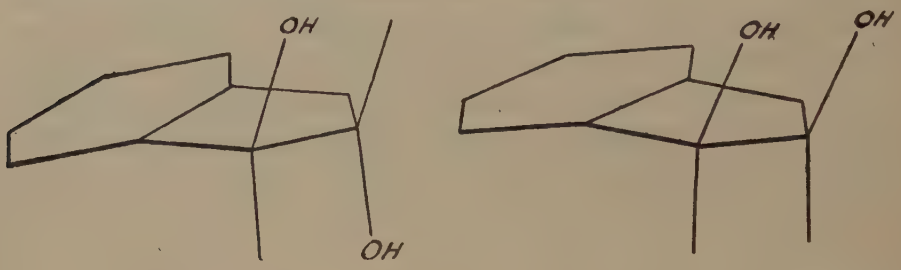
Indene oxide was hydrated as mildly as possible, that is to say at the ordinary temperature in aqueous solution with a very little acetic acid, and still we could isolate a considerable proportion of the trans isomer too. At this hydration likewise a valency of one of the carbon atoms that determine the configuration, is violated and a partial inversion takes place.

In judging the cis-trans isomerism in this case, the determination of the acidity is left out for the present, as the methods of investigation are not sensitive enough. The forming of an anhydride too cannot yield a good result here, because the bearers of the stereoisomerism are brought into play, which is *not* the case with the formation of anhydrides of acids, as of maleic or cumaric acid.

Here are only left 1. the resolution into optical antipodes, but this will not be easy and has never been successfully accomplished; 2. the formation of complex compounds, which has proved effectual with the sugars, as we came to know by it the configurations of α- and β-glucose, of α- and β-fructose and of α- and β-galactose. In the case under consideration too the last method has been to the purpose; the isomer melting at the lower temperature namely, increased the conductivity of boric acid, on the other hand the isomer with the higher melting point diminished it in some degree,

[1]) Versl. Kon. Akad. v. Wet **26**, 1272 (1918).

and from this the cis configuration could be deduced for the first mentioned diol. If this method had not come to the rescue, the case would have been almost hopeless, because a resolution into optical antipodes cannot enlighten us:



For it is evident that *both* isomers are asymmetrical and therefore can be resolved into optical antipodes.

It has been our intention to draw attention to the fact, that as soon as valencies are attacked of atoms which determine the stereoisomerism, the arrangement of the groups runs a risk of being changed. Of course the phenomenon going by the name of WALDEN's inversion ought also to be included here. In many cases the possible isomers are both formed and very often principally the one, which we should not expect.

This will not occur only with reactions as have been mentioned, by which stereoisomers are formed; in consequence of the formation of stereoisomeric substances, which can distinctly be discerned, the phenomenon was observed here as well as with the inversion of WALDEN. But it stands to reason that it is of a general character and that we may compose the rule:

During a chemical reaction, by which atoms are added, eliminated or substituted, there is always a chance that the arrangement is changed of the valencies of the atom or of the atoms, at which the reaction takes place.

It deserves further consideration to establish whether the arrangement around adjacent atoms or around remote atoms is disturbed, when such a change occurs with the valencies of some atom.

This is not probable fortunately, as it would highly aggravate our task to determine the configuration of compounds, for every relation between optically active substances would fail. Besides the formation of anhydrides of maleic or citraconic acid would be worthless and the differences, that may be observed in the influence of compounds

on the conductivity of boric acid, would lose all significance for the determination of the configuration.

Therefore, if this improbability be excluded and if we assume that an attack of the valencies somewhere in the molecule leaves unaltered the arrangement around the atoms, which are not immediately concerned, then we shall be able to obtain a solution in some apparently hopeless cases.

We have seen that with the two isomeric hexahydro-terephtalic acids a comparison of the dissociation constants does not answer the purpose; neither is resolvable into optical antipodes and besides from neither an anhydride could be obtained.

Of the Δ^2-tetrahydro-terephtalic acids (see accompanying diagrams)

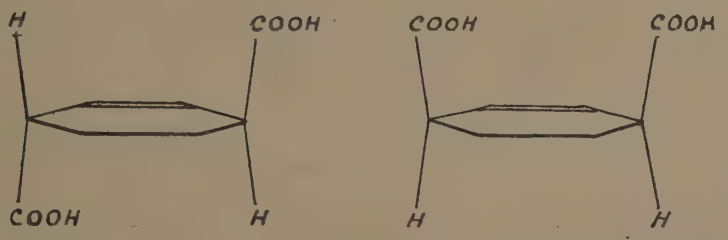


Fig. 2.

the trans acid should be resolvable into optical isomerides and it is thereby to be distinguished from the cis acid, which cannot be resolved.

Now it should oe possible to change these acids into the correspondent hexahydro-terephtalic acids by catalytic reduction, without altering the arrangement of the carboxyl groups and therefore the configuration of the last mentioned acids may be definitively established.

A case bearing an essential relation to this one, is:

Benzoquinone furnishes maleic acid by careful oxidation; from this we may conclude with rather great certainty, that this acid has the cis configuration, as this arrangement is contained in the quinone molecule and because at the elimination of the —CH = CH- group, the bonds that bear the isomerism, are not interfered with; if in the case of maleic and fumaric acid we were as badly equipped as with the hexahydro-terephtalic acids, then this mode of formation would have been of preponderant importance for the determination of the configuration.

Chemistry. — *"The Addition of Hydrogenbromide to Allylbromide"*. By Prof. A. F. HOLLEMAN and B. F. H. J. MATTHES.

(Communicated in the meeting of May 25, 1918).

In the many cases that in my laboratory I had trimethylene-bromide prepared by the introduction of HBr gas into allyl-bromide, I was struck with the fact that now an almost quantitative yield was obtained, now a much smaller yield, without our being able to indicate the cause of this varying yield. When now my assistant, Mr. DEN HOLLANDER, had obtained almost exclusively trimethylene-bromide in this addition in a very brightly lighted room, whereas a few years ago Mr. WUITE observed by the side of it considerable quantities of a product that boiled at a lower temperature (propylene bromide) in the ordinary work-room, the supposition suggested itself that daylight exerts an influence on this. Mr. MATTHES undertook to inquire more closely into this matter.

For this purpose a quantity of allyl-bromide was divided into two equal parts; one part was poured into an ordinary bottle, the other in a bottle that had been perfectly blackened on the outside with lacquer. The liquid in the ordinary bottle was exposed as much as possible to the sunlight during and after the introduction of HBr. Every time that no HBr was absorbed any more, it was closed, and left to itself till the next day. After some days no further HBr was absorbed. The blackened bottle was treated in the same way. The absorption of HBr took place a great deal more slowly here, so that the process had to be continued for some weeks, before complete saturation had been attained.

When the contents of the two bottles was afterwards subjected to distillation, the preparation from the ordinary bottle almost entirely went over at constant temperature and at the boiling point of trimethylene bromide. After distillation in vacuum its boiling point amounted to 167°.1 for 760 mm.

The contents of the other bottle, on the other hand, presented a very considerable boiling range, viz. from 100—190°. On fractionated distillation a fraction of about 7 gr., going over between 140°—150°, was obtained, while between 155° and 165° a fraction of 22 gr. went over. The former had about the specific gravity of propylene

bromide, viz. 1.9259 at 23°.2; the latter had the spec. gr. of trimethylene bromide, viz. 1.9801 at 23°.2. Between 100° and 105° a few drops had also been distilled, which were still unchanged allyl-bromide, as appeared from this boiling point. Hence the conclusion is that on addition of HBr to allyl-bromide in bright daylight trimethylene bromide is almost exclusively formed; in the dark, beside this compound as chief product, also pretty much propylene bromide.

Amsterdam, May 1918. *Org. Chem. Lab. of the University.*

Physics. — "*The variability with time of the distributions of Emulsion-particles*". By Prof. L. S. ORNSTEIN. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of March 31, 1917).

SMOLUCHOWSKI discussed this problem in different papers and gave a complete survey of his work in three lectures ad Göttingen.[1])

He deduced a formula for the average change of the number of particles in an element, which at the moment zero contains n particles. This formula is:

$$\overline{\Delta}_n = (v - n)\, P, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where P is the probability that a particle which lies in the element at the time zero, may have come outside in the moment t; whilst v is the number of particles which at a homogeneous distribution over the whole volume would come to lie in the element in consideration.

Also for the average square with a given number of particles n at the time zero SMOLUCHOWSKI gives a formula, viz.

$$\overline{\Delta^2 n} = [(n - v)^2 + n]\; P^2 + (n + v)\, P, \quad . \quad . \quad . \quad . \quad (2)$$

from which follows — if the average also is determined according to n —

$$\overline{\Delta^2} = 2\, v\, P.$$

These relations are deduced by SMOLUCHOWSKI with the help of calculations of probability, which "nach Ausführung recht komplizierter Summationen (yield) merkwürdigerweise das einfache Resultat".

It goes without saying, that it must be possible to attain such a simple result also by a less complicated method. That this is indeed the case I want to demonstrate in this paper. At the same time it will be possible to give some extension to the result.

1. Let us think the space divided into a great number of equal elements, which we shall mark by the indices $1 \ldots \varkappa \ldots k$. Let there be at a given moment $t = 0$ $n_1 \ldots n_\varkappa \ldots n_k$ particles in

[1]) Cf. Phys. Zeitschr. 1916, p. 557 and also Phys. Zeitschrift XVI. 1915. p. 323.

these elements. After a time t has passed these numbers have become changed. Let $p_{1\varkappa}$ then represent the chance that a particle which at the time $t=0$ is in the element 1, is found at the time t in the element $\varkappa$, and let $p_{\varkappa 1}$ represent the probability of the reversed transition. Then, if there is no predilection for any direction in the movement of the particles, it goes without saying that $p_{1\varkappa} = p_{\varkappa 1}$.

Further $\sum_{\lambda=1}^{\lambda=k} p_{\varkappa\lambda} = P$ if the sum is taken according to all values λ except $\varkappa = \lambda$, for the sum represents the probability that the particle has come after the time t in one of the $k-1$ other elements, i.e. outside the element $\varkappa$.

If an element λ contains n_λ particles the number of particles having passed from λ to $\varkappa$ in a given case will be $\Delta_{\lambda\varkappa}$. I shall now calculate first the average values of $\Delta_{\lambda\varkappa}$, $\Delta^2_{\lambda\varkappa}$ and $\Delta_{\lambda\varkappa}\Delta_{\mu\varkappa}$. The number of cases where $\Delta_{\lambda\varkappa}$ has the value s and thus $n_\lambda - s$ particles have remained in the element, amounts to:

$$\frac{n_\lambda !}{n_\lambda - s\,!\,s\,!}\, p_{\lambda\varkappa}{}^s\,(1-p_{\lambda\varkappa})^{\,n_\lambda - s} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

as is easily seen; to determine the three average-values this expression must be multiplied by s resp. s^2 and summed from zero to n_λ. Then after quite an elementary calculation of these finite sums, we find

$$\overline{\Delta_{\lambda\varkappa}{}^2} = p_{\lambda\varkappa}{}^2\,(n_\lambda{}^2 - n_\lambda) + p_{\lambda\varkappa}\,n_\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and

$$\overline{\Delta_{\lambda\varkappa}} = p_{\lambda\varkappa}\,n_\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

To determine the average of a double product we need only replace (3) λ by μ and s by t (where t represent the number of emitted particles in a definite case).

If the result obtained in this way is multiplied by (3) and summed with respect to ν from 0 to n_λ and with respect to t from 0 to n_μ, we find

$$\overline{\Delta_{\lambda\varkappa}\,\Delta_{\mu\varkappa}} = p_{\lambda\varkappa}\,p_{\mu\varkappa}\,n_\lambda\,n_\mu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

With the help of the relations (4), (5) and (6) Smoluchowski's formulae can now immediately be deduced. The change ${}_n\Delta_\varkappa$, i.e. the total change of the number of particles in the element $\varkappa$ may be represented by

$${}_n\Delta_\varkappa = \Delta_{1\varkappa} + \Delta_{2\varkappa} \ldots + \Delta_{k\varkappa} - (\Delta_{\varkappa 1} + \ldots \Delta_{\varkappa k}) \quad . \quad . \quad . \quad (7)$$

Now we can write $\Delta_\varkappa$ for $\Delta_{\varkappa 1} + \ldots \Delta_{\varkappa k}$, i.e. the total number of particles that leaves the element in the time t.

Then we must determine the average of (7) with constant n_ν,

while all possible values must be given to the number $n_1 \ldots n_\varkappa$ in the other elements. If now we first take the $n_1 \ldots n_\varkappa$ constant and determine the average, we find

$$\overline{{}_n\Delta_\varkappa} = p_{1\varkappa}\, n_1 + \ldots p_{k\varkappa}\, n_k - n_\varkappa\, P .$$

If then we proceed to determine the average according to $n_1 \ldots n_\varkappa$ and keep in mind that $\overline{n_1} = \ldots = \overline{n_\varkappa} = \nu$, we find

$$\overline{\overline{{}_n\Delta_\varkappa}} = \nu\,(p_{1\varkappa} + \ldots p_{k\varkappa}) - n_\varkappa\, P = (\nu - n_\varkappa)\, P .$$

In order to find $\overline{{}_n\Delta_\varkappa{}^2}$ we proceed in quite an analogous way, we bring (7) into the square. Then we find

$$\begin{aligned} \Delta_\varkappa{}^2 = \quad & \Delta_{1\varkappa}{}^2 + \ldots \Delta_{k\varkappa}{}^2 + \Delta_\varkappa{}^2 \\ & + 2\,\Delta_{1\varkappa}\,\Delta_{2\varkappa} + \ldots \\ & - 2\,\Delta_\varkappa\,(\Delta_{1\varkappa} + \ldots \Delta_{k\varkappa}) . \end{aligned}$$

If now we apply (5) and (6) and determine the average with given $n_1 \ldots n_k$ and $n_\varkappa$, we find

$$\begin{aligned} \overline{{}_n\Delta_\varkappa{}^2} = \quad & (n_1{}^2 - n_1)\, p_{1\varkappa}{}^2 + p_{1\varkappa}\, n_1 + \ldots + P^2\,(n_\varkappa{}^2 - n_\varkappa) + n_\varkappa\, P \\ & + 2\, n_1\, n_2\, p_{1\varkappa}\, p_{2\varkappa} + \ldots \\ & - 2\, n\, P\,(p_{1\varkappa}\, n_1 + \ldots p_{k\varkappa}\, n_k) . \end{aligned}$$

Here the average must be determined keeping constant $n_\varkappa$ with respect to n_1 etc. And we must bear in mind that $\overline{n_1{}^2} = \overline{n_2{}^2} = \ldots \overline{n_\varkappa{}^2} = \nu^2 + \nu$ [1]), that further $\overline{n_1} = \nu$ and $\overline{n_1 n_2} = \nu^2$. Consequently we find

$$\begin{aligned} \overline{\overline{{}_n\Delta_\varkappa{}^2} = \quad & (\nu^2 + \nu)\,(p_{1\varkappa}{}^2 + \ldots p_{k\varkappa}{}^2) \\ & + 2\,\nu^2\,(p_{1\varkappa}\, p_{2\varkappa} + \ldots \quad) \\ & - \nu\,(p_{1\varkappa}{}^2 + \ldots \quad) \\ & - 2\, n\, \nu\, P^2 + P^2\,(n^2 - n) + n\, P . \end{aligned}$$

The three first terms together yield $P^2\,\nu^2$. The result becomes thus

$$\overline{\overline{{}_k\Delta^2{}_n}} = \{\,(n - \nu)^2\, P^2 - n^2\, P^2\,\} + (n + \nu)\, P_\lambda$$

from which by determining the average according to n the relation

$$\overline{\Delta^2} = 2\,\nu\, P$$

arises.

2. The extension of the given formulae may be obtained to the case that the deviation of density in the various elements of volume are not independent, where however concerning the emission of the particles we must still presuppose independence of the events.

In order to introduce the correlation of the densities I make use of the function g, which was defined by Dr. ZERNIKE and myself. [2])

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[1]) We have $n_1 = \nu + \delta$, $\overline{n_1{}^2} = \nu^2 + 2\,\nu\,\overline{\delta} + \overline{\delta^2} = \nu^2 + \nu$.

$$\overline{n_1 n_2} = \overline{(\nu + \delta_1)\,(\nu + \delta_2)} = \nu^2 + \nu\,(\overline{\delta_1} + \overline{\delta_2}) + \overline{\delta_1\,\delta_2} = \nu^2 .$$

[2]) Chance deviations in density in the critical point of a simple matter. These Proc. XVII, 1914. p. 582.

If δ_0 is the deviation in density in a point $x=0,\ y=0,\ z=0$, then we get for the deviation of density δ in a point $x,\ y,\ z$:

$$\overline{\delta} = g(x, y, z)\,\delta_0\,dv \quad \ldots\ldots\ldots \quad (8)$$

where dv is the element of volume.

Further

$$\overline{\delta\,\delta_0} = g(x, y, z)\,\overline{\delta_0^2}\,dv = g(x\ y\ z)\,\varrho \quad \ldots\ldots \quad (9)$$

where ϱ is the number of particles per unit of volume.

We now have

$$\overline{{}_n\Delta_x} = n_1\,p_{1x} + \ldots n_x\,p_{kx} - n\,P.$$

Now $\overline{n_1} = v + \overline{\delta_1}\,dv_1$, if then we introduce (8) and consider $p_{\lambda x}$ as function of $x\,y\,z$, bearing in mind that $\delta_0 = \dfrac{v - n_x}{dv}$, we find

$$\overline{\overline{{}_n\Delta_x}} = (v-n)\left\{P + \int g_{\lambda x}\,p_{\lambda x}\,dv\right\}$$

The influence of the second part may become considerable with a strong correlation.

Also in determining $\overline{\overline{{}_n\Delta^2{}_x}}$ the correlation can be taken into consideration. Then in the first place we get the old terms, but moreover (9) yields still new terms in $\overline{n_\lambda^2}$, $\overline{n_\lambda}$ and $\overline{n_\lambda\,n_x}$, $\overline{n_\lambda\,n_\mu}$. These terms are:

$$2\,v\,(v-n)\int p_{\lambda x}\,g_{\lambda x}\,dv$$

$$-(v-n)\int p_{\lambda x}^2\,g_{\lambda x}\,dv$$

$$-2\,n\,P\,(v-n)\int p_{\lambda x}\,g_{\lambda x}\,dv$$

$$+2\,v\int p_{\lambda x}\,p_{\mu x}\,g_{\lambda\mu}\,dv_\lambda\,dv_\mu.$$

If then $\overline{\Delta^2}$ is determined, only the last term remains and a part of the term before last, so that we get

$$\overline{\Delta^2} = 2\,v\,(P + \int p_{\lambda x}\,p_{\mu x}\,g_{\lambda\mu}\,dv_\mu\,dv_\lambda + \int p_x\,g_{\lambda x}\,dv).$$

These considerations may also be applied, as least approximately, to the changes, which accidental derivations in density undergo in result of diffusion. Our formulae show then that close to a critical point the deviations in density as a result of their correlation, are not only stronger on the average, but also more strongly changeable.

Utrecht, March 1917. *Institute for Theoretical Physics.*

Physics. - *"On the Brownian Motion"*. By Prof. L. S. ORNSTEIN. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of December 29, 1917.)

VON SMOLUCHOWSKI [1]) observed that the function which gives the probability, that in the Brownian Motion a particle accomplishes a definite way in a given time is a solution of the equation of diffusion. For cases in which an exterior force also acts on the particles, he deduced a differential equation for the above-mentioned function of probability by a phenomenological method. Some time after Mr. H. C. BURGER [2]) deduced this differential equation following a method, which takes the essence of the function of probability more into consideration. Both deductions do not stand in direct connection with the mechanism of the Brownian motion; my object in this paper is to demonstrate, that starting from a relation which Mrs. DE HAAS—LORENTZ [3]) has used in her dissertation, to determine the average square of the distance accomplished, one is able to determine the function of probability of the Brownian motion. It is worth observing that the way in which different averages depend on the time may be calculated from the results obtained by Mrs. DE HAAS—LORENTZ by a slightly more careful transition of the limit than was necessary for the object she had put herself (viz. the determination of the stationary condition). First I want to determine these averages by a new method, which will offer the opportunity of demonstrating, that the opinion, from which Dr. A. SNETHLAGE [4]) starts in the theory of the Brownian motion that EINSTEIN's theory is in conflict with statistical mechanics, is incorrect.

Besides the function of probability for the distance I shall also deduce that for the velocity. The chain of thoughts which lead to

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[1]) Compare e.g. M. v. SMOLUCHOWSKI. Drei Vorträge über Diffusion, BROWN'sche Bewegung etc. Phys. Zeitschr. XVII p. 557 1916.

[2]) H. C. BURGER, Over de theorie der BROWN'sche beweging. Verslagen Kon. Ak. XXV p. 1482, 1917.

[3]) Mrs. Dr. G. L. DE HAAS—LORENTZ. Over de theorie der BROWN'sche beweging, Diss. Leiden 1912.

[4]) Miss Dr. A. SNETHLAGE, Moleculair-kinetische verschijnselen in gassen etc. Diss. Amst. 1917.

the results given below shows great similarity to the deductions which Lord RAYLEIGH [1]) gave utterance to already years ago. Kindred ways of regarding the stationary condition are also found in the work of Dr. FOKKER [2]) and M. PLANCK [3]).

§ 1. In the dissertation Mrs. DE HAAS—LORENTZ starts from the equation of motion for a emulsion particle, which she brings in the formula

$$m\frac{du}{dt} = -wu + mF \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Here u is the velocity of the particle, $w = 6\pi\mu a$ the resistance which according to STOKES' formula the spherical particle (radius a) would experience in a liquid with internal coefficient of friction μ. The force expended by the shocks of the molecules is divided into two parts, of which one is that according to STOKES, the second is quite irregular, so that $F = 0$. The determination of the average is to be understood in this way that it is to be taken at a given moment for particles which all have had the same velocity u_0 a time before.

Now we are able to integrate the equation (1), if we introduce $\frac{w}{m} = \beta$, we have

$$u = u_0 e^{-\beta t} + e^{-\beta t}\int_0^t e^{\beta t} F(t)\, dt \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where u_0 is the velocity at the time $t = 0$.

If then we determine the average of this equation in the way indicated, the result is

$$\bar{u} = u_0 e^{-\beta t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

or expressed in words: when we start from a great number of particles of given velocity, the average velocity decreases in the same way as with large spheres; the damping coefficient also is deduced in the same way from radius and coefficient of friction of the fluid. Let us now calculate also the average of the square of the velocity. For this we find:

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[1]) Lord RAYLEIGH, Phil. Mag. XXXII, p. 424. 1894. Papers III. Dynamical problems in illustration of the theory of gases.

[2]) Dr. A. FOKKER, Over de BROWN'sche beweging in het stralingsveld. Diss. Leiden, pg. 523, 1913.

[3]) M. PLANCK, Ueber einen Satz der Statistischen Dynamik u.s.w. Berl. Ber. p. 324. 1917.

$$\overline{u^2} = u_0^2\, e^{2\beta t} + e^{-2\beta t} \overline{\left\{ \int_0^t e^{\beta t}\, F(t)\, dt \right\}^2} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

In order to determine the integral in the second member we proceed in the following way. We write for it

$$\int_0^t \int_0^t \overline{F(\xi)\, F(\eta)}\; e^{\beta(\xi+\eta)}\, d\eta\, d\xi.$$

Now $\overline{F(\xi)\, F(\eta)}$ is only differing from zero if η and ξ differ very slightly, i.e. there is for short periods a correlation of the forces F. If we introduce $\eta = \xi + \psi$, it is allowed to replace η in the exponent by ξ and to split up the integral into a product of integrals according to ξ and ψ where we may integrate from $-\infty$ to $+\infty$. If then we assume

$$\int_{-\infty}^{+\infty} \overline{F(\xi)\, F(\xi + \psi)}\, d\psi = \vartheta \quad . \quad . \quad . \quad . \quad . \quad (4a)$$

which is a constant characteristic of the problem and if we perform the integration towards ξ, then (4) is transformed after substitution into

$$\overline{u^2} = u_0^2\, e^{-2\beta t} + \frac{(1 - e^{-2\beta t})\, \vartheta}{2\beta} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

When applying this equation for $t = \infty$, $\overline{u^2} = \frac{kT}{m}$ and thus we get

$$\vartheta = \frac{kT}{m}\, 2\beta$$

In the same way we are able to determine the average square of the distance accomplished. From (2) or by direct integration from (1) we get namely

$$u - u_0 = -\beta s + \int_0^t F\, dt$$

$$\beta^2\, \overline{s^2} = \overline{(u - u_0)^2} + \overline{\left\{ \int_0^t F\, dt \right\}^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

For the last integral we find in a quite analogous way

$$\vartheta\, t$$

If we calculate the first average with the help of (3) and (5) we obtain

$$\beta^2 \overline{s^2} = u_0^2 (1 - 2e^{-\beta t} + e^{-2\beta t}) + \frac{\vartheta}{2\beta}(-3 - e^{-2\beta t} + 4e^{-\beta t}) + \vartheta t \quad . \quad (7)$$

Consequently for very long periods we find

$$\overline{s^2} = \frac{2kT\vartheta}{\beta} = \frac{kT}{3a\mu} t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

which is the well-known formula for the average distance in the Brownian motion. If we determine the average of (7) with reference to all possible initial velocities and if we consider that $\overline{u_0^2} = \frac{\vartheta}{2\beta}$, we find for the average square of the distance accomplished as an arbitrary initial velocity :

$$\beta^2 \overline{s^2} = \frac{\vartheta}{\beta}(t\beta - 1 + e^{-\beta t}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (7a)$$

As long as βt is large in relation to $1 - e^{-\beta t}$ the formula of EINSTEIN is thus the right one. For the cases, considered in experiments, the lowest limit for t to be obtained in this way is of the order of 0.01 second.

§ 2. On the basis of statistical mechanics objections have been raised by Prof. J. D. v. D. WAALS JR. and Miss A. SNETHLAGE [1]) to the application of the division which has been applied to this case upon the example of EINSTEIN and HOPF in their treatment of another problem.

Starting from the supposition than in an "ensemble".

$$\overline{Ku} = 0$$

where K is the active force, they work out another fundamental formula viz. (with a slight variation in notation)

$$\frac{d^2u}{dt^2} = -\varrho^2 u + w \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where $\overline{w}$ has to been taken zero. We can again integrate this equation and obtain then

$$u = u_0 \cos \varrho t + \frac{\dot{u}_0}{\varrho} \sin \varrho t + \frac{1}{\varrho}\int_0^t w(\xi) \sin \varrho (t - \xi)\, d\xi \quad . \quad . \quad (10)$$

If taking the average we get :

$$\overline{u} = u_0 \cos \varrho t + \frac{\dot{u}_0}{\varrho} \sin \varrho t$$

The average velocity would in this way possess a definite period. If however we work out $\overline{u^2}$ we arrive at an incompatibility.

1) Cf. Versl. Kon. Ak. v. Wet. XXIV. 1916. p. 1272.

Because for $\overline{u^2}$ we get

$$\overline{u^2} = \left(u_0 \cos \varrho t + \frac{\dot{u}^0}{\varrho} \sin \varrho t \right)^2 + \frac{1}{\varrho^2} \overline{\left\{ \int_0^t w(\xi) \sin \varrho (t - \xi) \, d\xi \right\}^2} \quad . \quad (11)$$

For the integral, if again we make a double integral of it and if we introduce the constant θ

$$\theta = \int_{-\infty}^{+\infty} w(\xi) \, w(\xi + \psi) \, d\psi \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

we can write

$$\frac{\theta}{\varrho^2} \int_0^t \sin^2 \varrho (t - \xi) \, d\xi = \frac{\theta t}{2\varrho^2} + \text{periodical terms.}$$

Thus we find

$$\overline{u^2} = \frac{\theta t}{2\varrho^2} + \text{periodical terms} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

This formula shows that $\overline{u^2}$ increases indefinitely with the time, while it is evident according to statistical mechanics that $\overline{u^2}$ must approach $\frac{k T}{m}$.

Consequently if the equation (9) is treated as a differential equation we arrive at results which are not right [1]).

§ 3. Miss Dr. SNETHLAGE and Prof. Dr. J. v. d. WAALS Jr. have observed, that the theory of the Brownian motion must be in accordance with a general theorem of statistical mechanics. For the case that we consider a particle, that under the influence of the impacts of the molecules of the liquid executes a movement, the force which the molecules exercise does not depend upon the velocity, but only upon the coordinates. Consequently the product of force and velocity must on the average be zero, as well in a canonical as in a microcanonical as in a time ensemble. Now they are of opinion that EINSTEIN's formula comes into conflict with this. I shall demonstrate that this is only the case to a certain extent.

If we assume in a canonical (or micro-canonical ensemble) all systems selected in which the velocity of our particle at a point of time 0 is equivalent to u_0 and if then we follow this group of particles,

[1]) An analogous question is treated by M. PLANCK (Ann. der Phys. 1912. Bd. 37 p. 462) where it is demonstrated that the energy of a resonator subjected to the irregular field of black radiation increases in proportion to the time; the f of PLANCK agrees here with v. d. WAALS' u.

we can work out an average of every arbitrary quantity for the group of systems which after a time t has developed from the group considered at first. The value of the quantity considered varies for the different systems of our group (part ensemble), because the systems where at $t = 0$ the velocity of the particle is u_0, may still show considerable differences, so that e.g. the impulses which the particle gets will be widely different. I shall call this average the *case-average with a given initial velocity*. Moreover the velocity u_0 may be varied and again the case-average may be worked out and then by making u_0 run through all possible values all systems are taken into consideration in determining the average at the time t. If now the case-average of a quantity $g(u)$ for u_0 is $g(u_0)$ and if the number of systems of the group is $N(u_0)$ then — if N represents the total number of systems in the ensemble — the quantity

$$\frac{\Sigma\, N(u)\, g(u)}{N}$$

is the case-average for the entire ensemble.

However, as the ensemble is stationary the case average for a quantity is equal to the average of the corresponding quantity in the ensemble. If in particular $g(u)$ for every u is equal to zero, the average in the ensemble is also zero. I shall now demonstrate that if we start from EINSTEIN's formula the case average of Ku for every initial velocity u_0 is zero, and from this it follows immediately that EINSTEIN's formula does *not come into conflict* with the theory of the ensembles, more particularly that $\overline{Ku^e} = 0$, ($-e$ means determining the average of an ensemble, which — is used everywhere here for the case average).

EINSTEIN's equation comes into conflict with the theory of the ensembles if we select at $t = 0$ a group of particles with a given velocity u_0 from the ensemble. For if we determine the average of the equation it yields $m\overline{\frac{du}{dt}} = \overline{K} = -wu_0$, whilst according to the theory of ensembles K is independent of the velocity. If however we leave the selected group to itself and if we apply to its motion EINSTEIN's equation which is not right in the first moment, it is evident that in the long run the group moves in such a way that in the long run EINSTEIN's equation can be applied to it. Moreover from the group with particles with a given velocity u_0 those systems can be selected to which (1) applies. From what follows it becomes apparent that for this group in the long run the usual relations

with regard to the averages in a canonic ensemble become the right ones.

Instead of $Ku = 0$ we can also write $m\overline{\frac{du}{dt}u} = 0$ or $\overline{u\frac{du}{dt}} = 0$.

If now we multiply the EINSTEIN-HOPF equation by u and work out the case average, we get

$$\overline{u\frac{du}{dt}} = -\beta\overline{u^2} + \overline{uF}$$

Further we shall demonstrate that for sufficiently long periods the second member is identically zero.

For according to (5) we have got for the first term $-\frac{\vartheta}{2\beta}\beta$ or $-\frac{\vartheta}{2}$. We shall now determine the second average. For this purpose we multiply (2) by F and work out the average, and arrive at

$$\overline{uF} = \overline{u_0 e^{-\beta t} F} + e^{-\beta t}\overline{F\int_0^t e^{\beta t} F(t)\,dt}$$

In this formula the first average in the second member is zero. To determine the second average we must consider that F for the integral refers to a definite time t. And so only those parts of the integral where the argument differs only slightly from t yield distributions to the average. In the exponent we can again take the argument equivalent to t, so that we can write for the second term

$$\int_{t-\eta}^{t}\overline{F(t)\,F(t-\eta)}\,d\eta \quad \text{or} \quad \int_{-\infty}^{0}\overline{F(\xi)\,F(\xi-\eta)}\,d\eta$$

Now this integral is just half of the integral of (4a), as it covers half the region of integration, whilst the integrand is of course symmetrically with regard to ξ.

And so in the end we find for the second member identically zero as the two averages first neutralize each other. If now we take (5) into consideration for shorter periods the second member becomes

$$u_0^2 e^{-2\beta t} - \frac{\vartheta}{2\beta}e^{-2\beta t}$$

This result is also obtained by differentiating (4) with respect to the time.

The case average of $u\frac{du}{dt}$ for finite times not large with reference to $\frac{1}{\beta}$ is consequently not strictly zero. Now we can however determine

the average according to the initial velocity u_0 and so find the ensemble average of $u\frac{du}{dt}$. Then we obtain

$$u\overline{\frac{du}{dt}}^{e} = \left(\overline{u_0^2}^{e} - \frac{\vartheta}{2\beta}\right) e^{-2\beta t} = 0$$

as $\overline{u_0^2}^{e}$ possesses the equipartition value. Thus it is proved that also for short periods the average value of the case average does not come into conflict with statistical mechanics.

4. I shall now deduce the law of frequention for distribution of velocity. If we integrate the equation (1) for a short time τ, we can write for it

$$u - u_0 = -\beta u_0 \tau + x \quad \text{or} \quad u = u_0(1 - \beta\tau) + x \quad . \quad . \quad (14)$$

where $x = \int_0^\tau F(t)\,dt$ and $\overline{x^2} = \vartheta\tau$.

Now there is for x a law of frequention $\varphi(x)$, so that

$$\int_{-\infty}^{+\infty} \varphi(x)\,dx = 1 \quad , \quad \int_{-\infty}^{+\infty} x\varphi(x)\,dx = 0 \quad \text{and} \quad \int_{-\infty}^{+\infty} x^2\varphi(x)\,dx = \vartheta\tau \quad . \quad (15)$$

If now a particle starts with a given velocity u_0, the number of particles, for which in the time t the velocity lies between u and $u + du$, may be represented by

$$f(u_0, u\,t)\,du$$

or shorter

$$f(u, t)\,du$$

Let us now consider the distribution of velocity at the time $t + \tau$ and again fit our attention on the particles whose velocity lies between u and $u + du$. These particles have had at t a velocity u' in such a way that

$$u'(1 - \beta\tau) = u - x$$

or

$$u' = u(1 + \beta\tau) - x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

whilst an interval $du' = (1 + \beta\tau)du$ corresponds to the interval du). The number of particles that is at t in du' and at $t + \tau$ in du consequently amounts to

$$f(u', t)\,\varphi(x)\,dx\,du'$$

and thus we get

$$f(u, t + \tau)\, du = (1 + \beta\tau)\, du \int f(u', t)\, \varphi(x)\, dx \quad . \quad . \quad . \quad (17)$$

If now we work this out and retain the terms up to the first order in τ and if we take (15) into consideration and if after division by τ, we make τ approach zero, we obtain

$$\frac{df(u, t)}{\partial t} = \beta \frac{\partial}{\partial u}(u\, f) + \frac{\vartheta}{2} \frac{\partial^2 f}{\partial u^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

To the function of frequency for the velocity the extended equation of diffusion is thus applicable, where ϑ plays the part of coefficient of diffusion. The equation is quite of the same form as that for the Brownian motion under the influence of a quasi-elastic force ($-u$ or $-s$) (cf. also § 4). If we apply (18) to determine the stationary condition we have

$$0 = \beta \frac{\partial}{\partial u}(u\, f) + \frac{\vartheta}{2} \frac{\partial^2 f}{\partial u^2}$$

from which follows

$$f = C_1 e^{-\frac{\beta}{\vartheta} u^2} + C_2 e^{-\frac{\beta}{\vartheta} u^2} \int_0^u e^{\frac{\beta}{\vartheta} u^2} du.$$

This last term becomes infinite for $u = \infty$, consequently the integration constant must be taken $c_2 = 0$.

For the law of distribution we thus find the MAXWELL division of velocity quite independent of the initial condition. Moreover RAYLEIGH has carefully investigated this question for his particular example. He has deduced a similar equation for a particle in a highly rarefied gas, where only the constants β and $\frac{\vartheta}{2}$ have another meaning (cf. loc. cit.). It goes without saying that if one starts from the equation of V. D. WAALS-SNETHLAGE, one arrives at the conclusion that the division after long periods is *not* that of MAXWELL, and that there does not even exist a stationary division of velocity. And on this point also these investigators thus come into conflict with the statistical mechanics of GIBBS, which is the starting-point of their reasonings.

It may further be observed that for a particle beginning with a velocity zero, as long as u is still small with respect to the velocity of the particles, which collide against it, we get as RAYLEIGH has demonstrated

$$\frac{\partial f}{\partial t} = D \frac{\partial^2 f}{\partial u^2}.$$

For the change in velocity we get then at each impact according to RAYLEIGH

$$u' = u \pm 2q\,v,$$

where q is the relation of the masses of particles and molecules, v the velocity of the molecules. Now the problem treated by RAYLEIGH in this way may be connected directly with the theory of the function of probability for the way in the Brownian motion. If we take the velocity marked as vector, the terminal point is removed $\pm qv$ after every shock. The terminal point of the vector consequently executes a Brownian motion at least according to the scheme which is often given of it (cf. e.g. Mrs. DE HAAS—LORENTZ' dissertation). It is certainly remarkable how Lord RAYLEIGH had already so long ago deduced these results, which came to the foreground only by SMOLUCHOWSKI's work, which opened so many new views.

It may have its advantages now it has become apparent that EINSTEIN's formula is the right one to say something further on the kinetic mechanism. Let us first direct our attention to a single shock of a particle of a great mass with a particle of a small one. If the velocity for the first is before the shock u', after the impact u, the velocity of the small particle v and the relation of the masses q, where we have $q \ll 1$, then we get for every impact:

$$u = u'(1-q) \pm q\,v.$$

If we assume then that again and again after a time τ a collision takes place, then we have

$$\frac{u-u'}{\tau} = -\frac{q}{\tau}u' \pm \frac{q}{\tau}v$$

for every impact. We can only make a differential equation of this equation of differences by taking τ infinitely small, if q is of the same order infinitely small and then we get

$$\frac{du}{dt} = -\beta u \pm \beta v,$$

where F may be written for βv. Thus we see here by a (not very strict approach to the limit) EINSTEIN's equation arise as it were. If now we do not go to the limit, but avail ourselves of the following graphic representation, its meaning becomes even more clearly visible. On one axis we measure out the time (and to make things easier we take again equal intervals between the impacts), on the other the velocity. Between two collisions the velocity is then constant, at an impact the velocity suddenly jumps to another value and this jump consists in every case in two parts; one part proportional to the velocity of the particle before the shock with which

the velocity decreases and one part which may be either positive or negative (and in general may posses all sorts of values dependent upon the conditions of the impacts, which in the simple case investigated by RAYLEIGH is $\pm qv$). The velocity-time curve is thus a discontinuous curve. If the velocity has become large it has the tendency to become smaller by shocks owing to the first part, whilst the second part exercises no systematic influence in a contrary sense. If now we imagine a combination of curves drawn starting from a given velocity, EINSTEIN's equation will represent for each of these discontinuous curves the differential equation. At the same time if we introduce the curve $u = u_0 e^{-\beta t}$ into the scheme, this line will at all times be an average of the discontinuous velocity time-curves in the diagram.

§ 4. Finally I will deduce the function of probability for the Brownian motion under the influence of an external force. We take this force km, where k depends upon the place (s).

The equation of motion for our particle is then the following

$$\frac{du}{dt} = -\beta u + F + k \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

If now a particle has in the time $t = 0$ a velocity u^0, if in a time $t-\tau$ the velocity has become u' and a way s' is accomplished, and if u and s represent these magnitudes in a time t, we get

$$u - u' = -\beta (s - s') + \int_{t-\tau}^{t} F\,dt + \int_{t-\tau}^{t} k\,dt.$$

We now consider the time so small that the way accomplished in that time is small enough to treat K in the last integral which depends upon s as a constant.

We have thus

$$u - u' = -\beta (s - s') + \int_{t-\tau}^{t} F\,dt + k\tau \quad . \quad . \quad . \quad . \quad . \quad (20)$$

Now we want $\overline{\Delta s} = \overline{s - s'}$ and $\overline{\Delta s^2}$. In order to determine these we apply (3), this yields

$$\bar{u} - \bar{u'} = u_0 e^{-\beta t} (1 - e^{+\beta\tau})$$

as we have to take the mean value of Δs for all possible values of u_0 the average of $\bar{u}s$ being zero we get

$$\beta \overline{\Delta s} = k\tau \quad . \quad . \quad . \quad . \quad , \quad . \quad . \quad . \quad (21)$$

and in the same way

$$\overline{\Delta s^2} = \vartheta \tau \ldots \ldots \ldots \quad (22)$$

In order to arrive then at the differential equation for the function of frequency we reason again in the same way as before. Let $f(s,s_0 t)$ represent the chance that a particle that at the time 0 has the coördinate s_0 possesses at the time τ the coördinate s (with margin ds) where we determine the average according to the initial velocity. Now we follow the movement for a short time τ and build the function of frequention at the time $t+\tau$ from that on time s. If Δs again represents the mean deviation during the time τ, and $\varphi(\Delta s)$ the function of frequency, we know for this deviation that we have

$$\int \varphi(\Delta s)\, d\Delta s = 1, \quad \int \Delta s\, \varphi(\Delta s)\, d\Delta s = k\tau \text{ and } \int (\Delta s)^2 \varphi(\Delta s)\, d\Delta s = \vartheta\tau \quad (22a)$$

We then obtain

$$f(s, s_0, t+\tau)\, ds = \int ds' f(s', s_0 t)\, \varphi(\Delta s)\, d\Delta s \ldots \quad (23)$$

where $s' = s - \Delta s$.

If now we take (20) into consideration we find for the connection of ds' and ds

$$ds' = \left(1 - \frac{1}{\beta}\frac{\partial k}{\partial s}\tau\right) ds.$$

Developing according to (23) up to the first order with respect to τ, we find

$$\frac{\partial f}{\partial t} = -\frac{1}{\beta}\frac{\partial}{\partial s}(kf) + \frac{\vartheta}{2}\frac{\partial^2 f}{\partial s^2} \ldots \ldots \quad (24a)$$

If we introduce the value for ϑ and β we obtain

$$\frac{\partial f}{\partial t} = -\frac{m}{6\pi\mu a}\frac{\partial}{\partial s}(kf) + \frac{m}{6\pi\mu a^2}\frac{\partial^2 f}{\partial s} \ldots \ldots \quad (24)$$

This equation agrees with that of SMOLUCHOWSKI, if we take D (coefficient of diffusion of the Brownian motion $\frac{kT}{6\pi\mu a}$). The factor $\frac{1}{6\pi\mu a}$ is the ψ of SMOLUCHOWSKI i.e. the factor with which the force mk must be multiplied in order to calculate the velocity which in a stationary condition was caused by this force.

By DEBYE and his pupil Dr. TUMMERS [1]) a differential equation for

[1]) DEBYE, Zur Theorie der anomalen Dispersion. Verh. Deutsch Phys. Ges. X, p. 790.
J. TUMMERS, Over electrische dubbelbreking, Diss. Utr. 1914.

the function of the frequention of the axes has been deduced for the case of molecules (particles) which turn in a liquid, which is acted upon by an external couple and by a couple resulting from the molecular impacts. The deduction of the results obtained there follows immediately from our formulae. We need only split up the couple exerted by the molecular movement into two parts, the one $-\varrho\alpha$ (α be the angular velocity of the particle) $\varrho = 8\pi\mu a^3$ (a radius of the particle) and into a second part of which the average value (case average) is zero. For the motion of the axis we get then

$$P\ddot{\alpha} = -\varrho\dot{\alpha} + X$$

where P is the moment of inertia of the particle.

If we take $\dot{\alpha} = u, \frac{\varrho}{P} = \beta, \frac{x}{\varrho} = F$, we get for u equation (1), from which appears that the function of frequention can be deduced from a differential equation of the form (24a).

Finally it may be observed that it offers no difficulties to extend our considerations to the Brownian motion of coordinates in systems with an arbitrary number of degrees of freedom.

Utrecht, Dec. 8 1917. *Institute for Theoretical Physics.*

Physics. — "*The Theory of the Brownian Motion and Statistical Mechanics*". By Prof. L. S. ORNSTEIN and Dr. F. ZERNIKE. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of January 26, 1918).

Prof. J. D. v. d. WAALS Jr. and Miss. Dr, A. SNETHLAGE have raised objections derived from statistical mechanics against the usual deductions from EINSTEIN's formula of the Brownian motion. These objections may be formulated as follows:

Firstly: It is not right to introduce a resistance on an emulsion particle, which is proportional to the velocity of that particle, as according to a well-known result of statistical mechanics velocities and forces are independent of each other, as is appearent from

$$\overline{vK} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Still more clearly this independence is visible, if one considers that the above equation is not only applicable to the average over a canonical ensemble, but even for any group of systems from that ensemble for which the particle considered has a definite velocity v, so that for such a group $\overline{K} = 0$.

Secondly: It is not right to apply to this force of resistance the formula of STOKES, as it supposes that the liquid around the particle has a motion dependent upon the velocity of the particle. This comes into conflict with statistical mechanics, for these teach, that

$$\overline{v\, v_1} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where e.g. for v the velocity of the particle, for v_1 that of a molecule (both e.g. in the x-direction) in its neighbourhood may be taken. And so Miss SNETHLAGE has assumed for the calculation of the persistence of a particle in the Brownian motion, that the surrounding molecules have the usual Maxwellian distribution of velocity.

The authors mentioned have tried to give a theory of the Brownian motion which escapes these objections, by starting from (1). In what follows we want to show, that the equations (1) and (2) are much less far-reaching than it seems so that the objections to the usual theory may be considered to have fallen away, and on the other hand the reasoning given is proved not to be the right one.

In order to deduce the differential equation, which she wants to

put in the place of the equation of LANGEVIN-EINSTEIN, Miss SNETHLAGE differentiates equation (1) according to t. This yields

$$v\overline{\frac{dK}{dt}} = -\overline{K\frac{dv}{dt}} = -\frac{\overline{K^2}}{M} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

From which she rightly concludes that $\overline{\frac{dK}{dt}}$ is not independent of v. The nature of this dependence will be known, if for each value of v one knows the average $\overline{\frac{dK}{dt}}^v = F(v)$. Then there may be written for *one* system:

$$\frac{dK}{dt} = F(v) + w \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where w is an accidental quantity which on the average is zero ($\overline{w}^v = 0$).

If we want to determine $F(v)$ it is apparently necessary to consider the group of systems with a definite value of v. We shall further on indicate an average in such a "v-group", the same as above by $\overline{\quad}^v$, i. e. the average over the systems where in *one* definite moment v has a prescribed value, whilst the symbol $\overline{\quad}$ will indicate the average for the whole ensemble. As is proved by the following calculation equation (3) in not applicable, as (4) and (2), to every v-group in particular; and this Miss SNETHLAGE has left out of consideration.

Let K represent the force acting in the x-direction on the particle, v the velocity of this particle in that direction. Equation (1) is then found for the canonical ensemble, when K does not depend upon the velocities, and is exclusively a function of the coordinates $q_1 \ldots q_n$.

Let q_1 be the x coordinate of the particle, so that $q_1 = v$. Then we have

$$\frac{dK}{dt} = \frac{\partial K}{\partial q_1} v + \frac{\partial K}{\partial q_2} \dot{q}_2 + \cdots \frac{\partial K}{\partial q_n} \dot{q}_n$$

and for the average at definite v

$$\overline{\frac{dK}{dt}}^v = \overline{\frac{\partial K}{\partial q_1}}^v v + \overline{\frac{\partial K}{\partial q_2}}^v \overline{\dot{q}_2}^v + \text{etc.}$$

In order to reduce the last term we have made use of the well-known independence of the extension in velocity and configuration. These terms fall out because $\overline{\dot{q}_2}^v = 0$. The same independence has as its result that

$$\frac{\partial \overline{K^v}}{\partial q_1} = \overline{\frac{\partial K}{\partial q_1}}.$$

The last average is easily calculated from GIBBS' formulae.

$$\overline{\frac{\partial K}{\partial q_1}} = \frac{\int \frac{\partial K}{\partial q_1} e^{-\frac{\varepsilon}{\Theta}} dq_1 \ldots dq_n}{\int e^{-\frac{\varepsilon_q}{\Theta}} dq_1 \ldots dq_n}$$

Integrating by parts the denominater yields

$$\frac{1}{\Theta} \int K \frac{\partial \varepsilon}{\partial q_1} e^{-\frac{\varepsilon_q}{\Theta}} dq_1 \ldots dq_n$$

as the integrated part falls out ($\varepsilon = \infty$ at the limits).

Now

$$\overline{\frac{\partial \varepsilon}{\partial q_1}} = -K \quad \text{and therefore} \quad \overline{\frac{\partial K}{\partial q_1}} = -\frac{1}{\Theta} \overline{K^2}$$

Considering that $\Theta = M\overline{v^2}$, we obtain

$$\frac{\overline{dK^v}}{dt} = -\frac{v}{M\overline{v^2}} \overline{K^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

And so $F(v)$ has been found; equation (4) becomes

$$\frac{dK}{dt} = -\frac{\overline{K^2}}{M\overline{v^2}} v + w \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5a)$$

i. e. the very form given to this equation without further proof by v. D. WAALS and Miss SNETHLAGE. (Miss SNETHLAGE equation 24, sees however the note of these Proc. **24**, 1278 where a calculation remotely analogous to ours is found, without however our conclusions being drawn from it.)

The fact that $\frac{\overline{dv}^v}{dt} = 0$ and $\frac{\overline{dK}^v}{dt} = -\frac{v}{M\overline{v^2}} \overline{K^2}$ or $\frac{\overline{d^2v}^v}{dt^2} = -\frac{\overline{K^2}}{M^2\overline{v^2}} v$

has great inportance for the theory of canonical ensembles. If at a given moment one chooses a group of systems in which the suspended particle has a definite velocity-component v, then the formulae found are applicable to this group. Now one ought to consider, that, if one follows these systems in the time, the velocity of the particles does not remain the same for all of them, but that different velocities are going to arise. Moreover our formulae indicate that, if we take the average velocity a very short time τ after the selection of the group, it has become smaller than v. By

substitution of the above results in a series of TAYLOR we find namely:

$$\overline{v_t}^{v} = v\left(1 - \frac{\overline{K^2}}{2\,M^2\,v^2}\tau^2 \cdots\right)$$

Now it is remarkable that, if we follow the systems back into the time, i. e. determine the average for a moment $-\tau$ for a group where at $t=0$ the velocity of the suspended particle is v, exactly the same formula can be applied. So that we get a reversible process and questions analogous to the problem of the tops of H curves solved by EHRENFEST arise. Our reasonings consequently also give in principle how the objections may be put aside, which ZERMELO has raised to the statistical mechanics of GIBBS (as well as to the molecular theories of BOLTZMANN concerning the H theorem [1]).

The result obtained may shortly be formulated in this way: the properties of a group of systems, chosen so that in all of them the suspension-particle has a velocity v — a v-group —, are dependent on the time elapsed since the selection.

We may also ask now after the change of $\overline{vK}^{v}$ with the time for the v-group selected at the moment $t=0$. From the preceding calculation results that

$$\frac{d}{dt}\overline{vK}^{v} = \overline{\frac{dv}{dt}K}^{v} + v\,\overline{\frac{dK}{dt}}^{v} = \frac{\overline{K^2}}{M}\left(1 - \frac{v^2}{\overline{v^2}}\right) \quad . \quad . \quad . \quad . \quad (6)$$

from which it follows that the relation

$$\overline{vK}^{v} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

which is the right one for the moment in which the group was selected in the ensemble, is *not* right when this group is followed further.

It is true that the average for the last member of (6) for the ensemble is equal to zero, as is necessary with regard to the stationary character of the whole ensemble, which was already used in the deduction of (3).

Consequently we should be very careful in interchanging differentiation and determination of the average. So equation (5) will only be right for the first moment (just as (4)) and consequently also

[1] One ought to bear well in mind that the series-development given here is only right for a short time after the selection of the v-group from the ensemble. If one follows the group during a long time then the systems of which it consists will have spread themselves over the whole phase-extension with the density that belongs to a canonical ensemble.

For the importance of the EINSTEIN-LANGEVIN formula for this process compare the paper of one of us (ORNSTEIN), (preceding paper).

(5a), which accordingly *must not be looked upon as a differential equation*, Or: if we do consider (5a) right for later moments, we do not get in connection with it $\overline{w}^{v} = 0$, as it is made use of by Miss SNETHLAGE.

We are able to refute the second objection, viz. that statistical mechanics should not allow that the fluid moves with the particle in an analogous way. For this purpose we shall calculate the derivatives of

$$\overline{v\,v'}^{v} = 0$$

where v' is the x-velocity of an arbitrary molecule situated in the neighbourhood of the particle.

We have

$$\overline{\frac{d}{dt}\,v\,v'}^{v} = \overline{\frac{dv}{dt}\,v'}^{v} + v\,\overline{\frac{dv'}{dt}}^{v} = \frac{\overline{K}}{M}\,\overline{v'}^{v} + v\,\frac{\overline{K'}}{M'} = 0$$

as $\overline{v'}^{v}$ as well as $\overline{K'}$ are zero. Further

$$\frac{d^2}{dt^2}\,vv' = \frac{d^2v}{dt^2}\,v' + 2\,\frac{dv}{dt}\,\frac{dv'}{dt} + v\,\frac{d^2v'}{dt^2} = \frac{1}{M}\,\frac{dK}{dt}\,v' + 2\,\frac{KK'}{MM'} + \frac{v}{M'}\,\frac{dK'}{dt}.$$

The average of the first term yields

$$\frac{1}{M}\,\overline{\left\{\frac{\partial K}{\partial q}\,v\,v' + \frac{\partial K}{\partial q'}\,v'^2 + \ldots\right\}}^{v} = \frac{1}{M}\,\overline{\frac{\partial K}{\partial q'}}\,\overline{v'^2} = -\frac{\overline{KK'}}{M\Theta}\,\overline{v'^2} = -\frac{\overline{KK'}}{MM'}$$

and of the third term

$$\frac{v}{M'}\,\overline{\left\{\frac{\partial K'}{\partial q}\,v + \frac{\partial K'}{\partial q'}\,v' + \ldots\right\}}^{v} = \frac{v^2}{M'}\,\overline{\frac{\partial K'}{\partial q}} = -\frac{v^2}{M'}\,\frac{\overline{KK'}}{\Theta} = -\frac{v^2}{\overline{v^2}}\,\frac{\overline{KK'}}{MM'}$$

so that

$$\frac{d^2}{dt^2}\,\overline{v\,v'}^{v} = \frac{\overline{KK'}}{MM'}\left(1 - \frac{v^2}{\overline{v^2}}\right) \quad \ldots\ldots\ldots \quad (8)$$

For the change of v' with the time we have according to the preceding

$$\overline{\frac{dv'}{dt}} = 0$$

$$\overline{\frac{d^2v'}{dt^2}}^{v} = -\frac{\overline{KK'}}{MM'}\,\frac{}{\overline{v^2}}\,v$$

Now K is the sum of the forces in the x-direction, which all other particles exercise on the first, K' the corresponding sum for the second particle.

If we develop the product of these sums, we shall obtain the average of the product of action and reaction that may be assumed

to preponderate, so that we may expect that $\overline{KK'}$ is negative. The second derivative of v' consequently has the same sign as v, i.e. the movement of the surrounding matter with the particle, which does not exist at the moment of selection, arises after a short time. According to (8) there is on the average no question of a movement of the surrounding particles with the Brownian particle in an ensemble, as may be expected.

When we want to investigate statistically the qualities of a stationary system of molecules, we can make use of a statistically stationary ensemble and identify the qualities observed with the qualities of the most frequent system in this ensemble or with the corresponding averages.

The system that we consider at an investigation of the Brownian motion — a liquid with a particle suspended in it — is, it is true, not stationary, but all the same it changes only slowly: the moving particle changes its velocity only *slightly* by a *great number* of impacts. Consequently, in order to make use of ensembles for the study of the Brownian motion we must start from a "quasistationary" ensemble and deduce the qualities of the real Brownian motion from the properties of the most usual system in such an ensemble.

The calculations given show, that the groups chosen with definite v from a canonical ensemble do *not* form such quasi-stationary ensembles. However it seems probable to us that such a group, when we follow it a short time, will get to fulfill the requirements, though it will be difficult to show this by direct calculation. The v-group, which has become quasi-stationary at a later moment, would then correspond to the ensemble selected from the canonical ensemble, by selecting those systems in which the particle has already got the velocity v during a short time.

An indication with regard to the length of time required was found along another method by one of us in a former paper [1]).

The above quoted statistic-mechanical objections to the application of the law of STOKES thus probably have no justification for a real system, but only for the first moment of a v-group, i.e. at the very time when it cannot yet be made use of to represent the properties of a real system.

Groningen. *Utrecht, Institute for Theoretical Physics.*

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[1]) L. S. ORNSTEIN. l. c. — This time must namely be of the order of the time during which there is a correlation between the irregular impulses, i. e. $\overline{F(\xi)F(\xi+\tau)}$ differs from zero.

Physics. — "*The Scattering of Light by Irregular Refraction in the Sun*". By Prof. L. S. ORNSTEIN and Dr. F. ZERNIKE. (Communicated by Prof. W. H. JULIUS).

(Communicated in the meeting of April 27, 1917).

By the investigation of Dr. J. SPIJKERBOER in his dissertation "*Scattering of Light, and Distribution of Intensity over the Disc of the Sun*", the supposition of JULIUS [1]), that besides the scattering by the action of the molecules also the scattering by irregular bending of rays owing to accidental gradients of the optical density must play a part in the origin of the distribution of light over the disc of the sun, has been corroborated.

In this paper it is our object to show, that a mathematical treatment of the problem of the scattering of light by curving of rays is possible. For it is possible to put up an integral-equation for this phenomenon and to transform this with suitable and plausible suppositions into a differential equation with boundary conditions.

The problem treated here is the counterpart of the problem of molecular diffusion in a flat layer of gas, which was solved by SCHWARZSCHILD. The deduction of the integral equation resembles his train of thoughts, but in our case we have the advantage, that the peculiar nature of the problem allows that a differential equation can be deduced from it, which makes mathematical discussion so much easier. It seems to us, that the irregular reflection and the irregular double refraction may be treated in an analogous way, which is important for the theory of the extinction of liquid crystals.

In a medium, in which accidental gradients of the index of refraction arise, a ray of light will be curved in an irregular fashion. If a broad bundle of parallel rays runs through the medium, the different rays will be curved in different ways. And so, if the bundle is broad with regard to regions of a constant index of refraction, a bundle of initially parallel rays will be spread plume-shape. Now we fix our attention on the action of a volume-element on a ray, which goes in a given direction, and imagine that the nature of the irregularity of the index of refraction in the medium

[1]) W. H. JULIUS. Verslag Kon. Akad. v. Wet. **18**, 195 (1909) and **22**, 64—75 (1913).

is such, that after running through the element in question the diffusion of the rays has only taken place over a small cone. A characteristic difference with molecular scattering is, that with the scattering by refraction *not* a great part of the bundle goes on unimpeded and a small part spreads to *all* sides, but that the chief bundle itself gets continually broader.

And so, expressed in mathematical terms: let us follow light of a given direction over a length l, then, if this bundle has an intensity of one per unit of square, the intensity of the light which is found in a cone of the opening $d\omega$, of which the axis formed an angle α with the direction of incidence, will be possible to be represented after running through l by a function:

$$\chi(\alpha,l)\,d\omega \quad \text{or} \quad \chi(\alpha)\,d\omega$$

By making use of a particular image the form of the function χ may be determined. This form will be analogous to the law of errors; it is however unimportant for what follows. What is important is the supposition that the function χ possesses a perceptible value only for very small values of α.

If we take the meaning of χ into consideration, we see immediately that of course

$$\int \chi(\alpha)\,d\omega = 1$$

where the integral, just as everywhere else in what follows, must be taken over the whole unity sphere.

Now we shall deduce the integral equations for the intensity of radiation. Let $f(x, y, z, \vartheta, \varphi)$ represent the intensity of radiation in a point (x, y, z), whilst the direction is given by the angle ϑ with the x-axis and φ. If now we know the radiation in a point (x, y, z), we ask this quantity in a point that is situated l further in the direction of the ray ϑ, ψ. The coordinates of this point are:

$$x + l\cos\vartheta \quad , \quad y + l\sin\vartheta\cos\varphi \quad , \quad z + l\sin\vartheta\sin\varphi$$

And so the intensity of radiation may be represented by:

$$f(x + l\cos\vartheta \ , \ y + l\sin\vartheta\cos\varphi \ , \ z + l\sin\vartheta\sin\varphi \ , \ \vartheta \ , \ \varphi).$$

This intensity must now be equal to the intensity which by the bending of rays comes in the given direction. When ϑ' and ψ' are the angles which determine a ray in x, y, z, then, if α represents the angle of this ray with the ray ϑ, ψ, the intensity in the second point will also be given by:

$$\int \chi(\alpha)\, f(x, y, z, \vartheta', \varphi')\, d\omega'$$

so that the required integral equation is:

$$f(x + l\cos\vartheta, \ldots) = \int \chi(\alpha) f(x, y, z, \vartheta', \varphi')\, d\omega'.$$

Now it is easy to transform this integral equation into a differential equation, if we bear in mind that χ has only perceptible values for small values of α. We express by α the integration-element $d\omega'$ and the angle ψ, which the plane through (ϑ', φ') and (ϑ, φ) makes with that through $(\vartheta\varphi)$ and the x-axis. So that the value of $d\omega'$ is:

$$\sin\alpha\, d\alpha\, d\psi = \alpha\, d\alpha\, d\psi$$

For the difference of the angles ϑ and ϑ' and that of the angle φ and φ' we find going to the second order to α and after elementary reduction:

$$\Delta\vartheta = \vartheta' - \vartheta = -\alpha\cos\psi + \tfrac{1}{2}\sin\vartheta\cos\vartheta\,\Delta\varphi^2 = -\alpha\cos\psi + \alpha^2\frac{\cot\vartheta\sin^2\psi}{2}$$

$$\Delta\varphi = \alpha\frac{\sin\psi}{\sin\vartheta}.$$

Now we can develop in the integral $f(x, y, z, \vartheta', \varphi')$ with respect to $\Delta\vartheta$ and $\Delta\varphi$ and get in this way:

$$f(x, y, z, \vartheta, \varphi)\int\chi(\alpha)\, d\omega' +$$

$$+\frac{\partial f}{\partial\vartheta}\iint\Delta\vartheta\,\alpha\chi(\alpha)\, d\alpha\, d\psi + \frac{\partial f}{\partial\varphi}\iint\Delta\psi\,\alpha\chi(\alpha)\, d\alpha\, d\psi +$$

$$+\frac{1}{2}\frac{\partial^2 f}{\partial\vartheta^2}\iint(\Delta\vartheta)^2\,\alpha\chi(\alpha)\, d\alpha\, d\psi + \frac{\partial^2 f}{\partial\vartheta\partial\varphi}\iint\Delta\vartheta\,\Delta\varphi\,\alpha\chi(\alpha)\, d\alpha\, d\psi$$

$$+\frac{1}{2}\frac{\partial^2 f}{\partial\varphi^2}\iint(\Delta\varphi)^2\,\alpha\chi(\alpha)\, d\alpha\, d\psi$$

The first integral is equal to unity, the second yields

$$\frac{\pi}{2}\cot\vartheta\int\alpha^3\chi(\alpha)\, d\alpha,$$

the third is zero as well as the fifth, whilst the fourth and the seventh yield:

$$\pi\int\alpha^3\chi(\alpha)\, d\alpha \quad \text{and} \quad \frac{\pi}{\sin^2\vartheta}\int\alpha^3\chi(\alpha)\, d\alpha$$

Now we can introduce the mean value of α^3 according to

$$\overline{\alpha^3} = \int\alpha^3\chi(\alpha)\, d\omega = 2\pi\int\alpha^3\chi(\alpha)\, d\alpha$$

And thus we obtain at length, — if we also combine the first term of the second member with the first member and develop according to l — for the differential equation of the diffusion of light by irregular refraction:

$$\frac{\partial f}{\partial x}\cos\vartheta+\frac{\partial f}{\partial y}\sin\vartheta\cos\varphi+\frac{\partial f}{\partial z}\sin\vartheta\sin\varphi=\frac{\overline{\alpha^2}}{4l}\left(\frac{\cos\vartheta}{\sin\vartheta}\frac{\partial f}{\partial\vartheta}+\frac{\partial^2 f}{\partial\vartheta^2}+\frac{1}{\sin^2\vartheta}\frac{\partial^2 f}{\partial\varphi^2}\right)$$

For the case important in practice that f only depends on x and ϑ consequently:

$$\sin\vartheta\cos\vartheta\frac{\partial f}{\partial x}=\frac{\overline{\alpha^2}}{4l}\left(\cos\vartheta\frac{\partial f}{\partial\vartheta}+\sin\vartheta\frac{\partial^2 f}{\partial\vartheta^2}\right)\qquad[1].$$

For this case the boundary conditions are, if we have at $x=0$ a layer, which radiates according to the cosinus law and at d a plane layer through which no inward-radiation takes place:

$$f=c \quad \text{for:} \quad x=0 \quad \cos\vartheta>0$$
$$f=0 \quad \text{for:} \quad x=d \quad \cos\vartheta<0.$$

For $\vartheta=0$ and all values of x: f and $\frac{\partial f}{\partial\vartheta}$ continuous, $\frac{\partial^2 f}{\partial\vartheta^2}=0$; for

$\cos\vartheta=1$ or -1 $\quad\frac{\partial f}{\partial\vartheta}=0.$

It is worth observing that the diffusion is determined by the quantity $\frac{\overline{\alpha^2}}{l}$, i. e. the average square of diffusion per length-unity. This magnitude is specific for the problem, does not depend upon the length, as α^2 is doubled in doubling the length l. The magnitude is related to the nature of the irregularities. It is a constant which still may be different for different layers of the sun. The study of the distribution of intensity over the disc of the sun will be able to supply us with the knowledge of the average value of the characteristic constant of the sun.

Utrecht, April 1917. *Institute for Theoretical Physics.*

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[1]) For the two dimensional problem:

$$\cos\vartheta\frac{\partial f}{\partial x}=\frac{\overline{\alpha^2}}{4l}\frac{\partial^2 f}{\partial\vartheta^2}.$$

Meteorology. — *"On the diffraction of the light in the formation of halos. II. A research of the colours observed in halo-phenomena"*. By Dr. S. W. VISSER. (Communicated by Dr. J. P. VAN DER STOK).

(Communicated in the meeting of June 29, 1918).

In the first paper on the diffraction of the light in the formation of halos [1]) a survey of colours observed has been given on pag. 1175 taken from "Thunderstorms, optical phenomena etc. in Holland".

Prof. Dr. E. VAN EVERDINGEN however informed me, that these records are altogether insufficient because only a small number of colour observations are dealt with in "Thunderstorms". On his suggestion I have studied a number of records sent in to the "Koninklijk Nederlandsch Meteorologisch Instituut". In the first place I hope to have set right a neglect against the sincere voluntary observers of the Institute; in the second place this research gave valuable materials for the answer to the question how far and in what manner the diffraction works in the formation of halos.

In this paper a survey of the research is given; the results will be discussed and it will appear, that indeed the diffraction has an important influence on the refraction of light in ice crystals.

I started with all the colour records in the years 1913, '14 and '15. Then the research was extended to the years 1911, '12 and '13. In the first part I soon found, that great prudence was necessary. As an example I take the observations of "rainbow-colours". In the three years 1913—'15 I find "rainbow-colours" 12 times recorded by 9 observers. There are however 7 who have never sent in another record during all this time. They were evidently led by suggestion and fancy more than by observation power. The personal character also comes to the front. Therefore it was resolved to make a very careful selection and only to use records of those observers known to the Institute as wholly reliable. In this manner the notes are studied of eleven observers, who are mentioned in this paper with the numbers I tot XI.

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1) These Proceedings Vol. XIX.

Omitted were all incomplete observations and those about the moon. 550 Observations were at my disposal, divided over the six years as follows:

	1910	1911	1912	1913	1914	1915	Total
colour-records	125 (6)	107 (7)	114 (7)	81 (8)	66 (8)	57 (7)	550
total	473	480	399	283	325	377	2337
%	26	22	29	29	20	15	24

In parenthesis is mentioned the number of observers.

The row "total" gives the total number of records taken from "Thunderstorms".

The fourth part of all the notes gives reliable records.

31 Colours and colour-groups are mentioned, among which three very anomalous ones: blue IX; violet, red VIII; red, violet, green V. In the first communication are mentioned [1]) golden brown (red), yellow, green, violet (3 times by two observers); yellow, violet; golden brown, clear white, blue.

All the colour observations (divided over the two circles, the tangential arcs and the circumzenithic arc) are contained in the table I. (See table following page).

In the table the personal character comes out strongly.

144 observations of red by 10 observers (among which 115 of VII and IX), and 133 orange by 5 (among which 130 of V and X) where in most cases the same colour is meant, this clearly points to the personal estimation of this colour. The same is evident in the groups red-white and orange-white.

The table II also gives an idea of this individual opinion. (See table II page 122).

All the colour records of each observer, separately for the ordinary circle, the parhelion and the tangential arcs have been collected without further observations in this table. From this it appears, that the records of V, VII and X are limited to green (V has one observation of violet on a total number of 158). III also mentions blue, but never violet; VIII notes neither green nor blue, but in 22 records 12 times violet.

This phenomenon however interesting from a physiological point of view, greatly diminishes the value of the records, but without doubt green and blue colour shades often occur, as is further evident in the percentages of the separate colours in the following table (in which parhelion and tangential arc are taken together).

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[1]) l.c. p. 1330 seq.

TABLE I.

	circle 22	parhelion	tang. arc.	circle 46	circ. zen. arc.	total
white	51 (8)	7 (3)	1 (1)	—	—	59 (8)
red (brown)	119 (10)	14 (3)	9 (4)	2 (2)	—	114 (10) [1]
orange	123 (4)	7 (2)	3 (1)	—	—	133 (5)
yellow	15 (6)	4 (3)	1 (1)	—	—	20 (6)
blue	—	—	—	1 (1)	—	1 (1)
red, white (brown, white)	20 (6)	8 (1)	1 (1)	—	—	29 (6) [2]
orange, white	27 (1)	1 (1)	1 (1)	—	—	29 (2)
yellow, white	5 (2)	—	—	—	—	5 (2)
red, orange	4 (1)	—	—	—	—	4 (1)
red, yellow (brown, yellow)	10 (4)	2 (1)	1 (1)	—	—	13 (6) [3]
red, green	22 (3)	9 (5)	5 (2)	—	2 (2)	38 (5)
red, blue	10 (3)	2 (1)	2 (2)	1 (1)	—	15 (4)
red, violet	7 (1)	2 (2)	1 (1)	1 (1)	—	11 (2)
orange, yellow	1 (1)	—	—	—	—	1 (1)
orange, green	1 (1)	—	—	—	—	1 (1)
orange, violet	—	1 (1)	—	—	—	1 (1)
violet, red	1 (1)	—	—	—	—	1 (1) [4]
red, orange, white	—	1 (1)	—	—	—	1 (1)
red, yellow, white	1 (1)	1 (1)	1 (1)	—	—	3 (2)
red, green, white	1 (1)	—	—	—	—	1 (1)
red, orange, green	1 (1)	—	—	—	—	1 (1)
red, orange, violet	—	1 (1)	—	—	—	1 (1)
red, yellow, green	4 (3)	2 (2)	1 (1)	—	4 (1)	11 (3) [5]
red, yellow, blue	8 (3)	—	1 (1)	—	—	9 (4)
red, yellow, violet	1 (1)	1 (1)	—	—	—	2 (2)
red, green, blue	3 (2)	—	3 (2)	—	—	6 (2)
red, blue, violet	—	—	1 (1)	—	—	1 (1)
red, violet, green	—	1 (1)	—	—	—	1 (1)
red, yellow, green, blue	—	—	2 (2)	—	—	2 (2)
red, green, blue, violet	—	—	1 (1)	—	—	1 (1)
rd., or., yl., gr., bl., vi.	1 (1)	1 (1)	1 (1)	—	2 (1)	5 (3) [6]
	436	65	36	5	8	550

[1]) Among which brown 10 (2).
[2]) „ „ brown, white 11 (3).
[3]) „ „ brown, yellow 3 (1).
[4]) 1911, April 12: "on the outside reddish, inside violet". VIII. — April 23 VIII records: "on the outside common red".
[5]) An observation of an arc of Lowitz by HISSINK 1910, Sept. 7 at Zutphen was neglected.
[6]) Colours mentioned 2 times.
"All colours" once
"rainbow-colours" twice.

TABLE II.

	Circle of 22°							Parhelion							Tangential arc						
	w	*r*	*o*	*y*	*g*	*b*	*v*	*w*	*r*	*o*	*y*	*g*	*b*	*v*	*w*	*r*	*o*	*y*	*g*	*b*	*v*
I	1	3	—	4	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
II	—	4	—	1	—	—	—	-	1	—	—	1	—	—	—	3	—	—	—	4	—
III	2	21	—	5	2	15	—	—	—	—	—	—	—	—	—	3	—	1	3	1	—
IV	—	1	—	—	—	—	—	-	5	1	3	1	1	1	—	1	—	—	—	—	1
V	61	44	82	13	23	—	—	—	6	—	—	6	—	1	2	5	1	—	4	—	—
VI	1	6	1	4	1	4	2	—	—	—	-	—	—	—	—	1	—	—	—	-	—
VII	23	60	1	8	4	—	—	—	5	—	2	2	—	-	—	5	—	1	2	—	—
VIII	2	13	1	2	—	—	8	1	3	3	1	—	—	3	—	1	—	—	—	—	1
IX	11	50	—	7	1	—	—	14	23	2	4	1	2	2	2	6	—	3	—	1	—
X	3	4	73	2	1	—	—	2	1	6	1	1	—	—	—	—	3	1	—	—	—
XI	1	7	—	—	1	2	—	1	1	—	—	1	—	—	—	5	1	2	4	5	2
	105	213	158	46	33	22	10	18	45	12	11	13	3	7	4	30	5	8	13	11	4

	white	red	orange	yellow	green	blue	violet
circle 22°	17.9	36.3	26.9	7.8	5.6	3.8	1.7
parhelion, tang. arc	11.9	40.8	9.2	10.3	14.1	7.6	6.1

Surely the figures for violet are strongly flattered (21 observations of violet among which 12 of VIII). Without the records of VIII the percentages for violet are respectively about 0.3 and 3.8.

Evident is the great variety of colour of parhelion and tangential arc [1]).

By adding red and orange, green, blue, and violet the personal influences may be destroyed to some extent. Then I find

	white	red orange	yellow	green blue violet
circle 22°	17.9	63.2	7.8	11.1
parh. tang. arc.	11.9	50.0	10.3	27.8

Against a decrease of white and red we see an increase of the other colours. In more than $^1/_4$ of all cases colours are recorded approaching green and blue for the parhelion and the tangential arcs. This also happens with one in nine ordinary circles, where colours are made mention of.

[1]) Without doubt in the first communication I have slightly misunderstood PERNTER: the predomination of fixed crystal positions must at all events be very important.

Some colours and groups occur relatively often.

yellow; yellow, white	25 times;	6	observers
red, yellow; red, yellow, white.	16 „	6	„
red, green; red, blue; red, violet	64 „	8	„
red, yellow, green; red, yellow, blue; red, yellow, violet	22 „	7	„
red, green, blue	6 „	2	„
Spectrum colours	5 „	3	„

Green, blue and violet, to escape from personal influences, are again added.

The yellow takes a peculiar place. Yellow circles seem to occur. It is clear, that the yellow is often missing between the red and the green, but on the other hand it is often met with.

As regards the rainbow colours; 5 observations of 3 observers remain in six years.

Separate mention deserve the estimations of breadth by HEMMES at Arnheim in the ordinary circle and the tangential arc.

1911 Dec. 29	red $\frac{1}{2}°$ yellow $\frac{1}{2}°$ blue. $1°$
1912 Feb. 18 March 3 May 10	„ $\frac{1}{4}°$ „ $\frac{1}{4}°$ „ $\frac{1}{4}°$
March 8	„ $\frac{1}{2}°$ „ $\frac{1}{2}°$ especially at the top also blue.
1912 Jan. 6 1913 June 14	red $\frac{1}{4}°$, green $\frac{1}{4}°$ blue $\frac{1}{4}°$
1911 Dec. 3	red $\frac{1}{4}°$ yellow $\frac{1}{4}°$ green $\frac{1}{4}°$ blue $\frac{1}{4}°$.

The fact that the breadth strongly varies also appears from the detailed tables on the circumzenithic arc by BESSON [1]): 17 times on 91 arcs BESSON measured the colours. The distance from red to violet varied from $1\frac{1}{2}°$ to $3°$ ($1\frac{1}{2}°$: 3 times; $2°$: 6 times; $2\frac{1}{2}°$ twice; $3°$: 3 times). Three times blue and violet are wanting; among these is one arc, with which the breadth of the inside red to the green is $5°$. BESSON notes: "très large, très brillant".

These variations of breadth are very important for the theory of diffraction.

Summing up I find as the results of the research after eliminating the individual influences:

1. the pretty large wealth of colours,
2. the variation of colours,
3. the variation of breadth.

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[1]) Sur la Théorie des Halo's. Paris 1909. p. 62.

These results are not expected by the simple theory of refraction; they demonstrate the action of diffraction. It is these very properties which, for the rainbow, made the ordinary refraction-theory insufficient.

Evidently the conditions for the development of these phenomena of diffraction are present rather frequently. With great certainty this research has established the conclusions drawn in the first paper. The observations however difficult by the small power of the colours, which generally are to be taken as mixed colours, the records, however often delusive by personal influences sufficiently show, that in the formation of halos the diffraction plays an important part.

Mathematics. — "*Nouvelle démonstration du théorème de* JORDAN *sur les courbes planes*". By Prof. ARNAUD DENJOY. (Communicated by Prof. L. E. J. BROUWER).

(Communicated in the meeting of June 29, 1918).

Le théorème fondamental de JORDAN sur les courbes fermées peut s'énoncer ainsi:

Si les points d'un ensemble Γ *et ceux d'un cercle se correspondent réciproquement et continument, chacun à chacun, l'ensemble* Γ *divise le plan en deux régions.*

L'hypothèse faite sur Γ caractérise une *courbe* de JORDAN. Je me propose dans cette Note de donner une démonstration du théorème ci-dessus énoncé. Je rappellerai d'abord certaines définitions et résultats connus.

Nous caractérisons comme il suit les *côtés positif et négatif en un point* I *d'une ligne* HIK formée de deux segments de droite HI, IK, dont I est le seul point commun. Décrivons, dans le sens direct des rotations, un arc circulaire inférieur à 2π, de centre I, ayant son origine sur IK et son extrémité sur HI. Cet arc borne, avec HI et IK, un secteur de cercle ω. Soit L un ensemble continu, tel que, à l'intérieur d'un certain cercle c de centre I et de rayon inférieur à celui de ω, L et HIK aient seulement I en commun. Nous dirons que, au voisinage de I, L est situé du côté positif de la ligne HIK (ou du côté négatif de la ligne KIH) si les points de L intérieurs à c et distincts de I sont tous dans ω.

Il est aisé de voir que, *si* IK' *est du côté positif de* HIK, IK *est du côté négatif de* HIK'.

Si I est un point non extrême d'une ligne brisée λ simple (c'est-à-dire telle qu' un point quelconque de la ligne n'appartient à deux côtés différents que si ce point est origine de l'un et extrémité de l'autre), pour définir les côtés positif et négatif de λ en I, nous considérons un secteur de cercle analogue à ω, limité au côté (ou aux deux côtés) de λ contenant I, et ne rencontrant ancun autre côté de λ.

Soit P un polygone simple, défini avec son sens de parcours. On montre (voir *Comptes Rendus de l'Académie des Sciences de Paris*, 1911) que P divise le plan en deux régions (nous les appelons respectivement positive et négative, et les désignons par $P+$ et $P-$),

telles que tout continu joignant un de leurs points M au polygone P, atteint celui-ci du côté positif pour $P+$, du côté négatif pour $P-$. A et B étant deux points de P, la ligne brisée décrite en parcourant P selon son sens, de A à B est l'*arc direct* AB de P. L'*arc rétrograde* AB est géométriquement identique à l'arc direct BA, mais les sens de parcours des deux arcs sont opposés.

Pour démontrer le théorème de M. Jordan, nous utiliserons le lemme suivant :

Si, en parcourant une fois un polygone P dans un sens invariable, on rencontre successivement les quatre points A, B, C, D de ce polygone, et si (AC), (BD) sont deux continus joignant respectivement A à C, B à D, et dont tous les points, sauf A, B, C, D, sont dans une même région limitée par le polygone, ces deux continus ont au moins un point commun.

Supposons d'abord que (AC) soit une ligne brisée simple. On peut toujours choisir le sens positif de parcours de P, de façon que la région de P contenant (AC) et (BD), sauf leurs extrémités, soit $P+$.

Considérons alors le polygone π formé de l'arc direct CA de P, et de la ligne (AC) parcourue de A vers C. (AC) atteignant P en A et C du côté positif, l'arc direct AC de P s'écarte de π du côté négatif en A et C. Donc, D qui est sur cet arc est dans $\pi-$. Mais, P et π ayant en commun l'arc CA qui contient B, les côtés positifs de P et de π au voisinage de B coïncident. Donc le continu (BD) est, au voisinage de B, dans $\pi+$. On en déduit que (BD) rencontre π en un point différent de B. Comme (BD) ne rencontre pas l'arc CA, (BD) rencontre (AC).

Supposons que ni (AC) ni (BD) ne soient des lignes brisées simples. Si ces continus n'ont pas de points communs, leur distance minimum est un nombre positif α. On remplace le continu (AC) par une ligne brisée simple λ d'extrémités A et C, située, sauf pour ces deux points, dans $P+$ comme l'est (AC), et ayant tous ses points à une distance de (AC) inférieure à α. D'après la première partie de la démonstration, λ rencontre (BD). Nous aboutissons donc à une contradiction. Donc (AC) et (BD) se rencontrent dans tous les cas.

Nous déduirons de ce lemme une proposition essentielle.

Soit Γ une courbe de Jordan et O la circonférence de cercle correspondant ponctuellement à Γ. Si un point décrit O dans le sens direct, nous dirons que le point homologue de Γ décrit Γ dans le sens positif. On échange le sens positif de parcours de Γ en transformant le cercle O en lui-même par une symétrie par rapport à un de ses diamètres. Cela posé,

Si A, B, C, D sont quatre points d'un polygone simple P, et A', B', C', D' quatre points d'une courbe de Jordan *Γ ne rencontrant pas P, si (AA'), (BB'), (CC'), (DD') sont quatre continus deux à deux distincts contenant respectivement les points mis en évidence dans leurs désignations et n'en ayant aucun autre de commun avec P ni avec Γ, l'ordre des quatre points A', B', C', D' sur la courbe Γ, et celui de A, B, C, D sur P, l'une et l'autre parcourus dans le sens positif, sont identiques ou inverses.*

On voit sans peine qu'en échangeant entre elles, s'il en est besoin, les dénominations des couples associés A et A', etc., et aussi en modifiant le sens positif de Γ, la proposition serait en défaut dans le cas unique où, A, B, C, D étant rencontrés sur P dans leur ordre d'énonciation, on rencontrerait sur Γ successivement A', C', B', D'. Mais alors le continu (AC) formé de (AA'), de (CC') et de l'arc direct $A'C'$ de Γ, ne rencontrerait pas le continu (BD) formé de (BB'), de (DD') et de l'arc direct $B'D'$ de Γ. Or ces deux continus sont, à l'exception de leurs extrémités A, B, C, D l'un et l'autre dans la région de P contenant Γ. C.q. f. d.

Rappelons maintenant que si l'on forme une subdivision du plan en carrés égaux (γ) par deux familles de droites respectivement parallèles à deux directions rectangulaires, et, si l'on considère les ensembles formés par les carrés ne contenant, ni intérieurement ni sur leur contour, nul point d'un continu E, ces ensembles forment des domaines (réunion d'un continuum et de sa frontière; un continuum est un ensemble connexe dont tous les points lui sont intérieurs) dont chacun est limité par un polygone simple appelé *polygone d'approximation de E, relatif au quadrillage* (γ). Le sens positif d'un tel polygone π sera défini par la condition que E soit dans π^-.

Tout point H de π est situé sur l'un (on sur deux) des côtés d'un (ou de deux ou de trois) carré γ dont l'intérieur appartient à π^- et qui contient, intérieurement ou sur son contour, au moins un point de E. L'un de ces points-ci H', est tel que la distance HH' est minimum. Les points non extrêmes du segment HH' sont situés dans π^- et étrangers à E. D'ailleurs HH' est au plus égal à la diagonale de γ.

Cela étant, soient M et N deux points, distincts on non, appartenant à une même région limitée par Γ, et P, Q deux points de Γ tels que les segments MP, NQ aient en commun 1° avec Γ, uniquement les points respectifs P et Q, 2° entre eux, éventuellement et seulement certains de leurs points extrêmes (donc si M coïncide avec N, P est distinct de Q et inversement). M et N peuvent être joints par une ligne simple λ dont tous les points sont distincts de

Γ. Soit 4α un nombre inférieur à la distance de λ á Γ, et à la distance rectiligne $P\,Q$. ε étant moindre que α, considérons dans un quadrillage de côté ε le polygone π d'approximation de Γ, dont la région positive contient M et N. A partir de P et de Q, les segments $P\,M$, $Q\,N$ rencontrent π aux premiers points respectifs M_1 et N_1. Soit ϑ la plus grande des deux longueurs $M_1\,P$ et $N_1\,Q$. ϑ tend vers zéro avec ε. Si $\vartheta + \varepsilon < \alpha$, sur chacun des arcs directs $M_1\,N_1$, $N_1\,M_1$ de π, il existe des sommets, respectivement H, K, tels que les segments $H\,H'$, $K\,K'$ les joignant à leurs correspondants définis plus haut, ne coupent ni $M_1\,P$ ni $N_1\,Q$. Alors, d'après le lemme, H' et K' sont séparés sur Γ par P et par Q.

Cela posé, à un sommet H de l'arc direct $M_1\,N_1$ de π, faisons correspondre P ou Q ou H', selon que $H\,H'$ rencontre $M_1\,P$ ou $M_1\,Q$, ou ni l'un ni l'autre de ces segments. Alors, á la suite des sommets de l'arc $M_1\,N_1$ correspond une suite de points de Γ, tels que la distance de chacun d'eux au suivant est inférieure à $2\vartheta + 5\varepsilon$. Tous ces points sont sur un même arc $P\,Q$ de Γ, puisqu' aucun d'eux n'est sur l'arc $P\,Q$ contenant K'.

De même, sur ce dernier arc, nous pouvons former entre P et Q une chaîne de points, telle que la distance de chacun d'eux au suivant soit inférieure à $2\vartheta + 5\varepsilon$, chacun de ces points étant d'ailleurs distant de moins de 2ε d'un sommet de π. Nous déduisons de là les deux corollaires suivants:

1° *Toute région limitée par Γ admet pour frontière la totalité de Γ.*

Car la région contenant M et N admet pour frontière chacun des deux arcs $P\,Q$ de Γ.

2° *M et N étant dans une même région de Γ, P et Q étant sur Γ et les segments $M\,P$ et $N\,Q$ étant sans points non extrêmes communs, ni avec Γ, ni entre eux; quel que soit le nombre positif η, il est possible de trouver deux lignes brisées λ, λ' dont tous les points sont étrangers à Γ et situés à une distance inférieure à η, respectivement de l'arc direct $P\,Q$ et de l'arc direct $Q\,P$ de Γ, les extrémités de chacune des deux lignes λ, λ' étant, l'une sur $M\,P$, l'autre sur $N\,Q$.*

En particulier, si M, N et l'un des arcs $P\,Q$ sont intérieurs à un cercle c, on peut joindre M à N par une ligne brisée ne rencontrant pas Γ et intérieure à c.

De ces corollaires nous tirons les propositions suivantes:

1° *Toute courbe de* Jordan *admettant un arc rectiligne divise le plan en deux régions.*

En effet, soit I le milieu de l'arc rectiligne direct $H\,K$ appartenant à Γ et ω un cercle de centre I ne contenant aucun point de l'arc $K\,H$ de Γ. Le diamètre $H\,K$ divise ω en deux demi-cercles

ω_1 et ω_2. L'intérieur de ω_1 fait partie d'une même région r_1 limitée par Γ. De même l'intérieur de ω_2 appartient à une même région r_2 limitée par Γ. D'ailleurs, toute région limitée par Γ admet I pour point frontière, donc possède des points dans ω, donc dans ω_1 ou dans ω_2. Elle coïncide donc avec r_1 ou avec r_2.

Je dis que r_1 et r_2 sont distincts. Sinon, soient α_1 et α_2 deux points symétriques par rapport à I, et respectivement intérieurs à ω_1 et à ω_2. S'il était possible de joindre α_1 à α_2 par une ligne brisée simple λ ne rencontrant pas Γ, on pourrait choisir λ sans points communs avec le segment $\alpha_2\alpha_1$ en dehors de ses points extrêmes, et en ajoutant à λ le segment $\alpha_2\alpha_1$, on obtiendrait un polygone fermé ϖ. Le segment HK et le côté $\alpha_1\alpha_2$ de ϖ se coupent en leur milieu I. D'ailleurs HK ne rencontre plus ϖ. Donc, H et K sont dans deux régions différentes de ϖ. Donc, l'arc direct KH de Γ rencontre ϖ, et comme cet arc ne rencontre pas le segment $\alpha_1\alpha_2$, il rencontre λ, ce qui est contraire à l'hypothèse. La proposition est donc démontrée.

2° *Toute courbe de* JORDAN *divise le plan en deux régions.*

Soit J un point quelconque de Γ. Soit c un cercle de centre J et laissant à son extérieur un point K_0 de Γ. Il existe un cercle c' concentrique et intérieur à c, tel que, si P est un point de Γ intérieur à c', l'un des deux arcs PJ de Γ est intérieur à c. La même propriété est dès lors vérifiée pour l'un des deux arcs PQ, si P et Q sont à la fois sur Γ et dans c'.

Il est possible d'entourer K_0 d'un cercle c'' extérieur à c et tel que, si α et β sont deux points de Γ intérieurs à c'', l'un des deux arcs $\alpha\beta$ de Γ est extérieur à c. Le segment $\alpha\beta$ rencontre en général Γ en d'autres points que α et β, peut-être même en une infinité de points. Ceux-ci forment sur le segment $\alpha\beta$ un ensemble fermé. Soit HK un intervalle contigu à cet ensemble. Le segment HK est une corde de Γ. Ses extrémités seules font partie de Γ. L'un des deux arcs HK de Γ est extérieur à c. L'autre contient J. On peut, quitte à échanger les dénominations de H et de K, supposer que ce dernier arc est l'arc direct KH de Γ.

Soit Γ_1 la courbe de JORDAN obtenue en ajoutant à l'arc direct KH de Γ, le segment rectiligne HK. Dans c, Γ et Γ_1 coïncident, puisque ces deux courbes diffèrent uniquement par leurs arcs directs HK, l'un et l'autre extérieurs à c.

Γ_1 divise le plan en deux régions admettant l'une et l'autre J pour point frontière. Soient M et N deux points appartenant respectivement à ces deux régions et contenus dans c'. Joignons M et N à J. Soient, à partir de M et de N respectivement, P et Q les deux premiers points de rencontre obtenus avec Γ. Les segments

MP, NQ étant intérieurs à c', où Γ et Γ_1 coïncident, P et Q sont sur Γ_1 et les segments MP, NQ n'ont avec Γ_1 d'autres points communs que P et Q. MP et NQ n'ont pas de points communs entre eux, sauf éventuellement P et Q, si ces points coïncident avec J.

Je dis que tout point S étranger à Γ peut être joint à M ou à N par une ligne brisée ne rencontrant pas Γ. En effet, d'après le premier corollaire, S peut être joint à un point T intérieur à c' et étranger à Γ. T est, relativement à Γ_1, dans la même région que M ou que N. Soit R le premier point de rencontre à partir de T, du segment TJ avec Γ (et avec Γ_1, puisque TJ est dans c'). En vertu du second corollaire, on peut joindre T à M (ou T à N) par une ligne brisée $TT_1 M_1 M$ (ou $TT_1 N_1 N$) étrangère à Γ_1, et intérieure à c, puisque c contient les segments MP, NQ, TR, l'un des deux arcs PR et l'un des deux arcs QR. Comme l'arc direct HK de Γ ne pénètre pas dans c, la même ligne brisée est sans points communs avec Γ. Donc, Γ divise le plan en deux régions au plus.

D'ailleurs, M et N sont dans deux régions différentes de Γ, sinon on pourrait joindre M à N par une ligne brisée étrangère à Γ et située dans c. Donc, cette même ligne ne rencontrerait pas Γ_1, et par suite M et N seraient dans la même région de Γ_1, ce qui est faux par hypothèse.

Donc, Γ divise le plan en deux régions et deux seulement. Le théorème de Jordan est donc démontré. Nous avons au surplus obtenu un procédé pour définir le côté positif de Γ en un point J. On se donne c. On en déduit c', puis une corde HK de Γ, telle que ni cette corde, ni l'arc direct HK ne rencontrent c. La courbe formée par l'arc direct KH de Γ suivi de la corde HK, limite une région contenant le côté positif de la corde HK. Les points de cette région situés dans c' définissent le côté positif de Γ en J.

On montre sans difficulté que ce côté est indépendant de la corde auxiliaire choisie HK, et que les côtés positifs de Γ en tous ses points appartiennent à une même région limitée par Γ et que l'on peut appeler région positive de Γ.

Physiology. — *"On the spontaneous transformation to a colloidal state of solutions of odorous substances by exposure to ultraviolet light."* By Prof. H. ZWAARDEMAKER and Dr. F. HOGEWIND.

(Communicated in the meeting of April 26, 1918).

The literature contains a number of records concerning the spontaneous transformation to a colloidal state of substances whose molecules contain a noticeably large number of atoms (BLITZ[1]) colouring matters) or which are of a considerable molecular weight. (J. TRAUBE[2]) alkaloids). As one of us had noted the spontaneous transformation of eugenol in glycerin, when these substances are rapidly mixed up, and had been able to establish at the same time several details, we resolved to investigate more systematically the transformation of solutions of odorous substances in water, glycerin, and paraffin. After being rapidly mixed up, the solutions were allowed to stand for weeks and subsequently examined upon Tyndall's effect and observed ultramicroscopically[3]).

It appeared that the following solutions yield a strong Tyndall-effect.

In water	*In glycerin*	*In paraffin*
Eugenol	Eugenol	Anilin
Cressol	Safrol	Eugenol
Guaiacol	Creosote	Cumidin
Carvacrol	Nitrobenzol	
Citral		
Cumidin	Cressol	
Thymol	Apiol	
Hypnon		

In this table the odorous substances have been arranged according to their degree of transformation. In a number of cases the obliquely

1) BLITZ, Album J. v. BEMMELEN, 1910, p. 110 (boundary value between 45 and 55 atoms.)

2) J. TRAUBE, Int. Ztsch. f. Physik. Chem. Biol. Bd. I, p. 35, 1914 (boundary value between 208 – 275 molecular weight).

3) The examination upon Tyndall's effect was performed in the light-cone of a small electric arc-lamp, while watching the complete extinction of the obliquely

diffused light has been measured after the method of KAMERLINGH ONNES and KEESOM [1]). The values of the quantitative determinations in the series of the aqueous solutions are in the ratio of 43 : 39 : : 37 : 20 : 15 : 15 : 10; in the paraffinous solutions 23 : 18 : slight.

Besides the above solutions also the aqueous solutions of apiol, creosol, paraxylenol, anysaldehyd appeared to yield a markedly distinct effect. The Tyndal phenomenon is fairly distinct in old aqueous solutions of xylidin, orthotoluidin, chinolin, durol. A moderate effect we discovered of old aqueous solutions of methylcinnamylate, paratoluidin, salicylaldehyd, naphtalin, cumarin, toluol, anthranil-acid methylester, benzylbenzoate. A very slight effect was evinced by aqueous solutions of safrol, vanillin, anthracene, nitrobenzol. Tyndall's effect did not appear in old aqueous solutions of iron, heliotropin, moschus, isomuscon [2]).

The solutions were fully saturated. This is, however, not necessary for odorous substances with a strong tendency for transformation such as eugenol, cressol, guaiacol, carvacrol etc.

In glycerin solutions the phenomenon is of less frequent occurrence. We demonstrated the absence of Tyndall's effect in a number of old solutions in glycerin of odorous substances, which, when dissolved in water, became colloidal within a few days. Also in a solution in paraffin transformation occurs rarely.

When there is hardly any solubility, Tyndall's effect cannot be expected in the long run with odorous substances, but also, even when e.g. fluorescence shows us that molecules are thrown into solution, transformation to the colloidal state is sometimes lacking altogether, even when the solution has been standing for a long time. Such is the case with heliotropin. Eugenol is the substance that, both in water and in glycerin, attains a more intense colloidal condition than all other odorous substances examined. Also in paraffin eugenol becomes colloidal; anilin, in this solvent, still more so.

Generally speaking, odorous substances becoming intensely colloidal

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diffused light by means of a Nicol prism in the large apparatus of ZSIGMONDI. The solutions in glycerin, however, could not be taken up in an ordinary cuvette, the stuff with which the quartz windows are fixed, being soluble in glycerin. In this case we therefore used Zeiss' paraboloid condensor, or a Leitz' darkground-condensor-cuvette.

[1]) KAMERLINGH ONNES and KEESOM, Acad. Amst. 29 Feb. 1908.

[2]) The list of odorous substances that are transformed spontaneously has since been lengthened considerably. Also the alkaloids that become at length colloidal in aqueous solutions, are very numerous. It is interesting to contrast with them the crystalloid condition of nearly all solutions of antipyretica (non-alkaloids).

have a greater molecular weight than those that are not transformed or hardly so; again, the former generally bring about a more considerable lowering of the surface-tension of water. For the solutions examined upon their Tyndall effect the number of droplets decreased in an orderly manner. Calling the number of droplets for pure water 49, that of eugenol is 90, crissol 80, carvacrol 80, citral 72, thymol 72, guaiacol 70, cumidin 65, hypnone 54. This series corresponds approximately with the one holding for Tyndall's effect. On the whole there is an orderly decrease in the power to produce a lowering of the surface tension between air and water, similar to that of the power to bring about a colloidal condition of the saturated or half-saturated solution.

When examining our solutions ultramicroscopically while standing for days and weeks, at various intervals, the number of submicrons appears to augment [1]) to the detriment of the amicrons, which formed the base of the cone. In strong colloid solutions there ultimately appears a precipitate, as in the case of eugenol. By the addition of $^1/_2$ n. sodium-carbonate solutions the markedly opalescent fluid at once becomes rather more translucent, in which process amicrons re-appear, this time to the detriment of the spontaneous submicrons previously formed.

Prior to and subsequent to transformation the surface-tension of the solution is approximately equal (with a eugenol solution 1 : 1500 fresh 67 and old 67 droplets for the stalagmometer volume). Also the smell-intensity is the same before and after transformation. Upon this basis we feel justified in terming the transformed odorous solutions "suspensoids". Exposed in the usual way in an U-tube to the action of a constant electric current, the particles in these suspensoids were all moved towards the anode. It follows then that the particles themselves must be negatively charged. The arm with the + pole was getting more opalescent, the one with the — pole cleared up.

After reversal of the current the previous state was restored. Likwise the previous intensity of Tyndall's effect is restored by mixing the contents of the two arms. The following table gives the quantitative relations of the light-intensities of the Tyndall effect of the solutions,

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[1]) The fluids, the colloidal as well as the fresh-prepared control fluids, were instantly filtered in the cuvette through a paper filter. Consequently with pure water only half a dozen submicrons at the most were discernible in a microscopic field. With water a base of amicrons was altogether lacking, similarly with the fresh control-fluids; but in the saturated or partly saturated solutions that through standing had been changed into suspensions, we discerned besides a base of amicrons a very large number of submicrons in active Brownian movement.

tabulated above, after allowing a current to pass through for one hour:

INTENSITY OF THE OBLIQUELY DIFFUSED LIGHT.

	Initially	At the — pole	At the + pole
Eugenol.....	37	33	41
Guaiacol.....	37	29	35
Cressol.....	24	19	23
Carvacrol.....	20	16	24
Citral	20	16	22
Cumidin	15	12	18
Thymol.....	15	10	16
Hypnone.....	10	slight	16

After displacement of the micellae in the suspensoids through the influence of the current, the surface tension in the arm of the positive pole appears to become somewhat less than in the arm containing the negative pole.

NUMBER OF DROPLETS (CALLING THAT OF WATER 49).

	Previously	At the — pole	At the + pole
Eugenol.....	90	87	89
Carvacrol.....	84	79	80
Cressol.....	80	78	79
Citral	73	71	74
Thymol.....	72	70	71
Guaiacol.....	70	70	71
Hypnone.....	55	54	56

When heating an aqueous eugenol solution 1 : 1200 beyond 40°, the opalescence decreases, whereas it returns on cooling and after a few days becomes more intense than before. Below 30° no change occurs, even when the solution is maintained at 30° for 24 hours.

Similarly a colloidal solution of eugenol in glycerin appeared to be much less opalescent on hot summerdays than on cooler days preceding or following.

The gradual transformation of solutions of odorous substances beginning with the formation of amicrons, that develop into submicrons, appears to be largely influenced by light. When kept in the dark, the process is slow in aqueous solutions. There are even several substances, e.g. chinolin, in which it does not appear at all, but in which it comes forth distinctly in daylight. It should also be observed that the effect of ultra-violet light is much stronger than that of daylight [1]).

When exposing a eugenol-solution in a quartz test-tube at $^1/_2$ m. distance from the light of a mercury quartz lamp, opalescence is attained within half an hour, which otherwise is not arrived at in a fortnight. An electric arc-lamp has the same effect in a smaller degree. This quickening of transformation does not occur when the quartz-tube is enclosed in stanniol-paper. The same was observed with all other solutions. Even a heliotropin solution, ultramicroscopically empty, shows, after half an hour's radiation, numerous micellae.

Besides by the ordinary light-waves and the ultra violet rays, odorous substances can also be rendered colloidal by radiation with radium kept in vitro. In order to ascertain this we took two perfectly equal glass cuvettes with parallel walls, each filled with saturated odorous solution. In one of the cuvettes a closed glass tube was inserted, in which 200 mgrs of a mixture of radium- and barium-bromide containing 0,18 % $RaBr^2$. If the experiment was performed with a saturated heliotropin solution, the control fluid remained ultramicroscopically empty, whereas the solution, in contact with the radium tube, showed in 24 hours a base of amicrons and 10 submicrons per microscopic field. Something similar occurred in a short time also with the other odorous solutions of the table, though with every following substance of the series more time was required to obtain a difference in dispersity between the radium-cuvette and the control-cuvette.

Not only the admitted electro-magnetic waves of the visible light, the ultraviolet light and the γ-rays of the radium, but also the mechanical energy is competent to give to a fresh-prepared, saturated multitomic odorous solution the energy needed for an amount of surface-energy sufficient for the formation of numberless amicrons and submicrons, to be observed in the gradually developed suspensoid. By shaking the fluid forcibly, transformation is largely promoted. In

[1]) Besides opalescence also fluorescence is generated. We are unable to decide whether there is any relation between light electricity and the observed highly accelerated transformation to a colloidal state. Cf. Hellwachs on Light-electricity in Marx's Hab. d. Radiol. Vol. III p. 438.

a heliotropin solution e.g. that remained free from submicrons, even after standing for months, they appear in a rather large number directly after the old solution was shaken for some time in the closed cuvette. The same occurs with glycerinous solutions. Eugenol poured on glycerin without shaking renders the latter non-opalescent in five days. When it is vigorously shaken, however, the fluid is rendered slightly opalescent, and colloidal in the real sense of the word. It also retains its suspensoidal character in the subsequent phase of the process.

It is not likely that chemical energy should also come into play, since the process also takes place in chemically all but indifferent fluids, such as paraffin, though it must also be added that entire deoxidation of paraffin inhibits transformation also in ultraviolet light. However, there must be still another unknown source of energy, apart from the radiation of light and the mechanical energy, which supplies the newly generated micellae with surface-energy, with or without the aid of oxygen, since eugenol solution enclosed in a leaden casket, kept in utter darkness, becomes undoubtedly

TRANSFORMATION TO A COLLOIDAL STATE OF AQUEOUS SOLUTIONS IN THE ANILIN-SERIES.

	Molec. weight	Number of Atoms	Tyndall's effect
Anilin.....	93	14	hardly distinguishable
Toluidin.....	107	17	rather distinct
Xylidin.....	121	20	" "
Cumidin.....	135	23	distinct

ID. IN THE BENZOLSERIES.

	Molec. WEIGHT	NUMBER OF ATOMS	Tyndall's effect
Benzol.....	78	12	hardly distinguishable
Toluol.....	92	15	little distinct
Xylol.....	106	18	
Pseudocumol....	120	21	little distinct
Durol.....	134	24	rather distinct

suspensoidal within a few days. However, to obtain this, large dissolved molecules are required. This is clearly shown when comparing the terms of an homologous series inter se.

Odorous substances never have very large molecules. [1]) Therefore, there will never be an extremely strong tendency to form amicrons, subsequently submicrons, as soon as the supply of energy that may pass into surface-energy, is established. This accounts for the process being hitherto unobserved. But when working with much larger molecules, we may readily presume that the process of transformation is highly facilitated, and will show itself very distinctly, whenever electromagnetic waves, mechanical energy, or the unknown source of energy, suggested above, are present, from which the particles to be formed, derive their surface-energy.

[1]) The odorous substances examined by us, had a molecular weight between 78 and 199; the number of their atoms amounted to from 14 to 27, on the understanding that no multiple of the chemical formula should be taken.

Chemistry. — "*The Passivity of Chromium*". (Third Communication). By Dr. A. H. W. Aten. (Communicated by Prof. A. F. Holleman).

(Communicated in the Meeting of March 23, 1918).

When it is tried to explain the results communicated in the foregoing papers [1]) we should in the first place consider the possibility that the hydrogen (or oxygen) present in the surface layer of the metal, has a certain influence on the phenomena.

The phenomena, that render it probable that the hydrogen present in the surface layer of the metal promotes the activity, are among others the following.

When a piece of Goldschmidt chromium, which contains little hydrogen, is placed in a feeble acid or in very dilute sulphuric acid, it does not go spontaneously into solution with generation of hydrogen. When the chromium is, however, cathodically polarized, so that hydrogen is generated in consequence of this, the chromium goes also into solution as chromousion. When the current is broken, also the dissolving as chromousion stops, when the acid is diluted enough. In more concentrated acids, especially in hydrochloric acid, and also at higher temperatures in diluted acids, the dissolving accompanied by hydrogen generation, begins spontaneously after a short time.

From the fact, that the cathodic polarisation causes the solution of the chromium, we may conclude that the hydrogen charge that the metal acquires in this case, is the cause of the activity. At the same time it follows from this that a hydrogen charge corresponding to gaseous hydrogen of one atmosphere is not sufficient to activate chromium, for in this case the activity would have to continue to exist when the current is broken. At that moment, and also some time after, the metal has, namely, a hydrogen charge that is at least equal to one atmosphere, and yet the going into solution ceases spontaneously. The activity disappears even when the cathodic polarizing current is not broken, but only sufficiently weakened [2]). Flade [3]) denies this statement of Rathert, but describes

[1]) These Proc. XX, p. 812, 1119.

[2]) Rathert. Zeitschr. f. physik. Chemie **86**. 567, (1914).

[3]) ibid. **88**. 569 (1914).

an experiment that proves about the same thing. He found, namely, that a passive electrode in diluted sulphuric acid could be cathodically polarized to a feeble hydrogen generation without becoming active.

The behaviour of chromium in acids can be derived from figure 1.

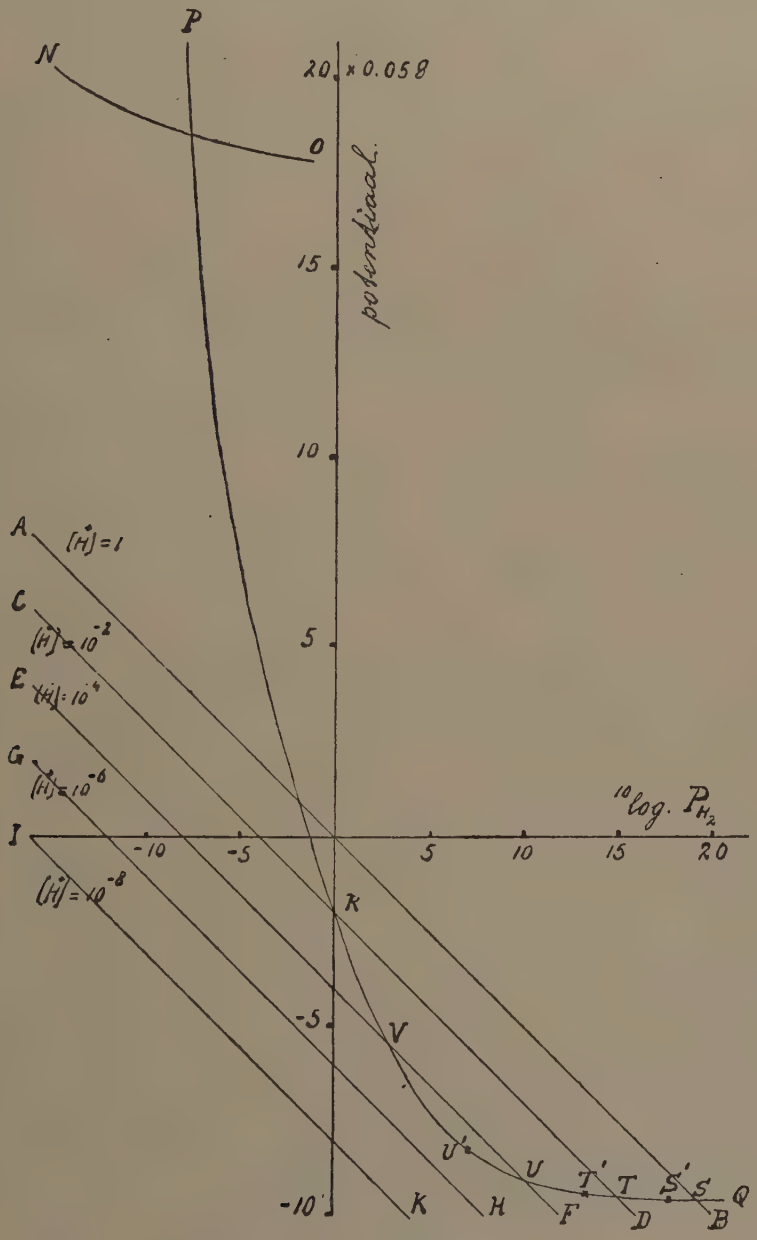

Fig. 1.

The 10 log of the hydrogen pressure has been plotted on the abscissa, the potential on the ordinate. The line AB indicates the

hydrogen charges which an electrode acquires for different potentials when the concentration of the hydrogen ions in the solution is 1.

The same thing is given by the line CD for a hydrogen ion concentration 0.01 etc. These lines are nothing but the graphical representation of the potential of the hydrogen electrode.

Let us now assume that the potential of a chromium electrode in a solution of a given chromium concentration is determined by the density of the hydrogen charge, and can be represented by the line PQ in figure 1. There is little to be said about the course of this line; only on increasing hydrogen charge this line must draw near to a limiting value, which represents the real potential of equilibrium of chromium.

This latter supposition, that the electrode presents a chromium potential, which c.p. is only dependent on the density of the hydrogen charge, goes slightly further than the usual hydrogen hypothesis, according to which the hydrogen would only accelerate the setting in of the equilibrium. According to our conception a certain chromium potential corresponds to a given hydrogen charge. This supposition may seem improbable considered in itself, without it an explanation by the aid of the hydrogen hypothesis is not possible in my opinion. In what way the chromium potential comes about here, will not be discussed.

When we now take a chromium electrode with a gas charge 1, then the potential of this is R, according to figure 1. If this electrode is placed in a solution, which is 0.01 n. of acid, it can generate from it exactly hydrogen of one atmosphere. In consequence of the overvoltage no hydrogen will be generated, but the chromium will not lose its gas charge either. Hence the potential remains unchanged. When the same chromium is brought in an acid in which the concentration of the hydrogen ions is $= 1$, the chromium at the potential R can develop hydrogen in this acid to a pressure of 10^4 atm. In consequence of the increase of the hydrogen charge the potential now descends below R, this causes the hydrogen charge to increase, and thus the potential will continue to descend. The lowest value that *can* be attained, is S. This value *need* not be reached, however. It can only exist for a hydrogen charge of 10^{20} atm., and this is only possible when there is a very great overvoltage for hydrogen generation at chromium.

It appears therefore from this, that chromium with a hydrogen charge 1 will spontaneously activate, when placed in an acid which is stronger than 0,01 n. If the acid is weaker, the chromium does not spontaneously become active. In 10^{-4} n. acid a hydrogen charge

of 10^{-4} atm. corresponds to a potential R, and the hydrogen charge of chromium does, therefore, not become stronger of its own accord. When, however, this chromium is cathodically polarized in 10^{-4} n. acid, the hydrogen charge increases, the chromium potential decreases. If this falls below V, the chromium can be activated further spontaneously till the potential has become U. By stronger cathodic polarisation the potential can become lower than U; when the current is broken the potential will, however, have to rise again up to U. The potential itself will not stop at U, but become higher. If the hydrogen generation is sufficiently vigorous to maintain a sufficient gas charge on the chromium, the potential can remain between V and U. Then the chromium remains active. When the hydrogen charge becomes smaller than corresponds with V, the potential rises above V, and the activity disappears. Not only when the current is broken can the potential rise above V; it is also possible that this already takes place in case the polarizing current is weakened. When e.g. with vigorous cathodic polarisation the gas charge becomes greater than V, the gas charge can become smaller than V when the hydrogen generation becomes feebler, and the activity will disappear. This is the above described phenomenon of RATHERT. It is likewise possible that with very weak cathodic polarization the hydrogen charge does not become great enough to lower the potential below U. Then the metal remains passive in spite of the cathodic polarization (FLADE).

The most negative potentials that the chromium can spontaneously assume in 1 n. 0.01 n. and 0.0001 n. acid, are accordingly S, T, and U. These will, however, not be reached, because a very great overvoltage would be required for it. In reality the potentials S', T', and U' will e.g. be observed.

The above given considerations account, therefore, sufficiently for the spontaneous activation of chromium in acids, and the activation by cathodic polarization, also in connection with the strength of the acid.

Chromium becoming more easily active in hydrochloric acid than in sulphuric acid or in other acids, there must exist a specific activating action of the chlorine ions. This comes to this that a smaller gas charge is required for the activation in hydrochloric acid, and that the line PQ must therefore be drawn more to the left for hydrochloric acid. The same thing applies for higher temperatures.

It appears then also from figure 1, that chromium can only remain strongly active in a liquid in which it develops hydrogen, and, therefore, maintains its gas charge itself. When now a fresh electrode

of electrolytic chromium, which contains a great quantity of hydrogen, is placed in a solution of chromous-sulphate, as described in the first paper, this will at first present a strongly negative potential in consequence of the great hydrogen charge. When the chromium is left in contact with the solution, it loses its hydrogen at the surface. The potential shifts along the line QR in the direction of R. The potential rises then to $E_h = -0.27$ V, as was communicated in the first paper.

This is, therefore, probably the *chromium* potential that the metal presents for a hydrogen charge 1, because the chromium will cede hydrogen to the solution till its pressure has become one atmosphere.

When such an electrode is now cathodically polarized in chromous-sulphate, hydrogen is generated. The chromium regains its hydrogen charge, and with it its active potential.

By the aid of figure 1 the phenomena for cathodic polarisation are, therefore, to be explained in a simple way. Also the activating action of the anodic polarization on electrolytic chromium can be accounted for by the aid of these considerations, when the diffusion of the hydrogen in the metal is taken into account.

When the chromium has been electrolytically separated, it has a high hydrogen content, of which we assume that it is the same throughout the entire thickness of the layer. When in figure 2 DF

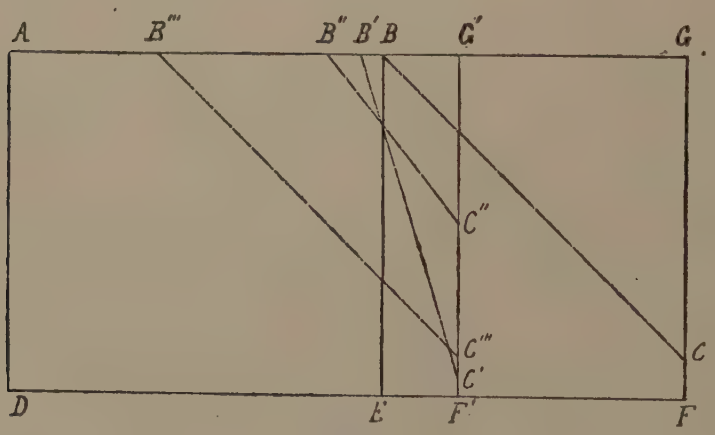

Fig. 2.

represents this thickness and we plot the concentration of the hydrogen normal to it, this is represented by a horizontal straight line AG. The line GF represents the surface of contact of the chromium with the liquid. On account of the great hydrogen content in the boundary surface the chromium will possess a very active potential. When

the chromium is left in contact with the liquid, the hydrogen present in the boundary surface GF, will for the greater part pass into the solution, or escape in gas form. This causes the concentration of the hydrogen at the boundary surface to become smaller.

In consequence of this the hydrogen diffuses from the metal towards the boundary surface, and after a certain time the concentration of the hydrogen in the chromium will be represented by the line ABC. In the part AB the concentration has remained unchanged, in BC the concentration has changed through diffusion. We shall call the layer EF, in which the diffusion is perceptible, the diffusion layer. The chromium now presents a potential which is determined by the size of FC.

When we now polarize anodically, the first consequence will be, that the hydrogen concentration at the boundary surface FC becomes smaller. This will at any rate be the case when the solution used is so little acid, that the hydrogen potential corresponding to a given hydrogen charge, is more negative than the chromium potential of the same hydrogen charge. This applies therefore to those parts of the hydrogen lines (AB, CD, etc.) that lie under the chromium line PQ in fig. 1. For in case of anodic polarization, the potential of the metal will here lie further above the equilibrium potential of the hydrogen than above that of the chromium, so that the hydrogen will dissolve to a greater extent.

At the same time chromium goes into solution. Hence the boundary layer GF shifts to the left, and gets e.g. at the place $G'F'$. The thickness of the diffusion layer has now become smaller, and the concentration of the hydrogen in this layer is represented by $B'C'$. Now the hydrogen charge at the boundary surface is $F'C'$, hence smaller than before the anodic polarization. When the strength of the current is kept constant, a stationary state will set in, in which $F'C'$ is constant, and also the concentration gradient in the diffusion layer.

When the strength of the current is increased, this stationary state will be another, i.e. so, that $F'C'$ is smaller and the concentration gradient of the hydrogen in the diffusion layer greater than in case of smaller strength of current, because the diffusion layer is thinner.

During anodic polarization the potential will be more positive than before, because the hydrogen concentration at the boundary surface is smaller. When the current is broken, the hydrogen will quickly diffuse towards the boundary surface in consequence of the great concentration gradient in the thin diffusion layer. This causes the hydrogen charge at the boundary surface to rise, e.g. to $F''C''$.

Besides, the diffusion layer becomes thicker again, as the metal no longer dissolves; the point B', therefore, gets in B''. C'' must lie higher than C, because at C'' more hydrogen diffuses towards the boundary surface than at C on account of the slight thickness of the diffusion layer. This hydrogen must also pass into the liquid more rapidly, which is only possible when $F'\,C''$ is greater than $F\,C$.

When the value C'' has been reached, the hydrogen charge at the boundary surface will decrease again through the continual passing of hydrogen into the liquid, and through the supply of hydrogen from the metal going more slowly, because the diffusion layer becomes thicker. At last a stationary state is again reached, which is equal to the state before the polarization, and in which the hydrogen charge of the boundary surface is $F'\,C'''$, the concentration of the hydrogen in the diffusion layer $B'''\,C'''$.

The greater the density of the current, the smaller will be $F'\,C'$, the thinner will be the diffusion layer, and the higher therefore will C''' lie.

Hence the following particulars will be observed for the potential of electrolytic chromium. When electrolytic chromium with a fresh surface is brought into an electrolyte, the hydrogen charge at the boundary surface is great, FG, and the potential strongly negative. When this chromium is left in contact with the liquid for a long time, the boundary surface of the metal loses part of its hydrogen, the hydrogen charge falls to FC, and the potential becomes more positive. When we polarize anodically, the hydrogen charge decreases to $F'\,C'$, the potential becomes, therefore, still more positive. When the current is now interrupted, then the hydrogen charge rises to $F'\,C''$, the potential becomes much more negative, but gradually the hydrogen charge decreases again to $F'\,C'''$, and the potential rises to the value that it showed before the polarization.

This course is quite in concordance with what was drawn in figure 7 of the second communication.

Accordingly the potential reaches a minimum which is the deeper as C'' lies higher, hence as the strength of the current is greater and consequently the diffusion layer is thinner.

When the strength of the current is very small, and the diffusion layer is thick, it may occur that C'' does not get above C''', and that the potential does not pass through a minimum, as is the case with the line for $1mA$ in figure 7 of the second communication.

It is clear that the phenomena for anodic polarization will, therefore, chiefly be determined by the hydrogen content of the metal.

These phenomena being different for chromium on copper, on

silver, and on gold i.e. so that the potentials for chromium on copper are the most negative, it must be assumed that chromium deposited on copper contains more hydrogen than chromium on silver, and this more than chromium on gold.

In the same way the existence of a retrogressive current potential line can be explained, as has been drawn in figure 11 of the second communication. These lines refer to the formation of chromate, and we shall, therefore, have to assume that also the potential of chromate formation will be dependent on the hydrogen content. This dependence is e.g. given by the line NO in figure 1.

Here too, in case of anodic polarization the concentration of the hydrogen at the boundary layer will be small, hence the potential high. On increasing current density the diffusion layer becomes thinner, so that in case of interruptions of the current by the commutator the hydrogen charge at the boundary surface *after* the current has been broken will be the greater as the current density was greater.

Hence for greater current density the potential is more negative after the current has been interrupted than for small current density. Moreover it is clear that the retrogressive current potential line can only be found when we work with a commutator. When the potential is measured with continual passage of the current, the potential is the more positive as the current density is greater, because then only the hydrogen charge at the boundary surface is to be reckoned with as it is *during* the polarization.

Accordingly the activation *after* anodic polarization can be satisfactorily accounted for by means of the hydrogen theory.

It remains, however, to explain the phenomenon that on anodic polarization of electrolytic chromium and of activated chromium of GOLDSCHMIDT, the potential becomes more negative also during the passage of the current.

An explanation of this may be arrived at when it is borne in mind, that not immediately after the current is broken or started the state in the diffusion layer is stationary.

When in figure 3 BC represents the concentration of the hydrogen in the diffusion layer of a piece of chromium which has been in contact for a long time with an electrolyte, the hydrogen at the boundary surface has the concentration FC. When this electrode is now anodically polarized, the concentration of the hydrogen will descend to $F'C''$ in consequence of this. Now the concentration of the hydrogen in the diffusion layer will have the course $B'C''$. This will be the state when the current has just been started, and the

boundary surface has, therefore, been only little shifted inward. When the passage of the current is continued, the boundary surface moves more inward, and when it has reached $F''' G'''$, a stationary state

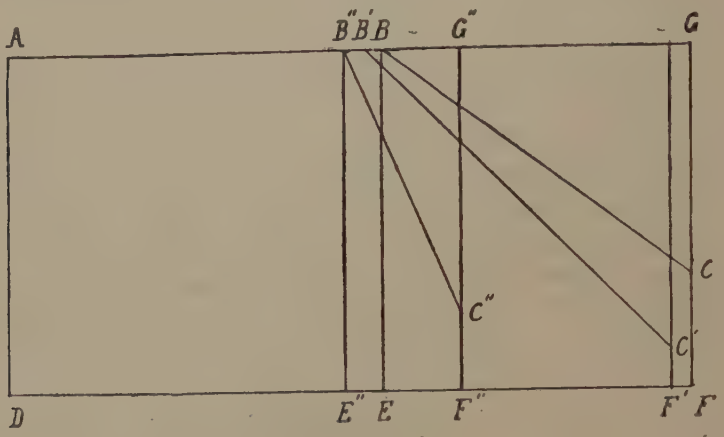

Fig. 3.

will have been reached, in which the thickness of the diffusion layer and the concentration gradient of the hydrogen is stationary. The former is smaller and the latter is greater than when the current had just been started; consequently also the hydrogen charge at the boundary surface $F''' C'''$ can now be greater than at first. The course of the potential as function of the time will, therefore, be as follows. Before the polarization the electrode is comparatively active, corresponding to the hydrogen charge $F C$. When the current is put on, the potential rises in consequence of the decrease of the hydrogen charge. On continued passage of the current the potential descends again, because the hydrogen charge becomes greater again in consequence of the diffusion layer becoming thinner.

This is what was observed for the anodic polarization of electrolytic chromium, and also of GOLDSCHMIDT chromium which is activated in molten $ZnCl_2$ or $KCl + NaCl$. Also with chromium of GOLDSCHMIDT which has been activated in strong HCl, the same phenomenon is observed. Nevertheless there exists quantitatively a great difference between these two kinds of chromium. With electrolytic chromium the activation proceeds much more quickly during the passage of the current than with GOLDSCHMIDT chromium which has been activated in $ZnCl_2$, and with this again more quickly than with GOLDSCHMIDT chromium that has been activated in hydrochloric acid. For this last the potential continued to become more and more negative for hours with constant strength of the current. For electrolytic chromium this continued only for a few minutes. The difference

in the duration of the phenomenon may be attributed to a difference in the hydrogen content of electrolytic chromium and GOLDSCHMIDT chromium. The former can bear a much stronger current already at the beginning of the anodic polarization than the latter. In consequence of this the displacement of the boundary surface GF to $G''F''$ goes much more quickly for electrolytic chromium than for chromium of GOLDSCHMIDT, hence also the activation on anodic polarization proceeds more quickly for electrolytic chromium.

As has been described in the second paper, a piece of GOLDSCHMIDT chromium that has become active through anodic polarization, can not bear the same strength of current any more when the current has been broken for some time, though the potential is then much more negative than immediately after polarisation. This, too, can be accounted for by the diffusion of the hydrogen in the metal. Before the polarization the concentration of the hydrogen in the diffusion layer is represented by BC in figure 4. When the electrode is

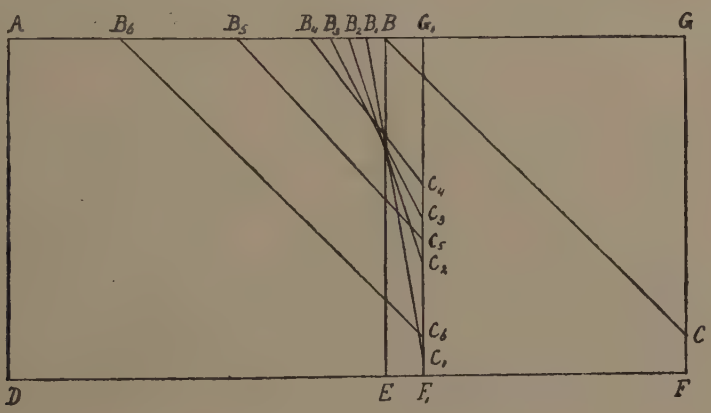

Fig. 4.

anodically polarized, and the strength of the current is slowly carried up, a stationary state will be reached after some time, for which the concentration of the hydrogen in the diffusion layer, which has now become a good deal thinner, is represented by B_1C_1. When the current is interrupted, the hydrogen concentration at the boundary surface rises in consequence of the great gradient of concentration. Besides the thickness of the diffusion layer increases, which extends inwards in the metal, and is no longer dissolved from outside. The course of the concentration of the hydrogen in the diffusion layer is now successively represented by B_1C_1, B_2C_2, B_3C_3, B_4C_4, B_5C_5, and B_6C_6. With B_4C_4 the concentration of the hydrogen at the boundary surface is greatest, the potential, therefore, most negative.

When we now anodically polarize with the same strength of current as when the hydrogen concentration was represented by B_1C_1, the hydrogen charge at the boundary surface will now descend below C_1, since the thickness of the diffusion layer is now so much greater than immediately after polarization, and the diffusion of hydrogen accordingly proceeds so much more slowly. In consequence of this the chromium gets a more positive potential. In this way it is, therefore, explicable that the chromium can bear a stronger current when this is again put on immediately after the interruption than when the current has remained broken for some time, though in the latter case the potential is more negative in current-less condition. It now also appears that there is no immediate connection between the potential of a chromium electrode in current-less condition, and the possibility of its becoming passive. The former is namely determined by the density of the hydrogen charge at the boundary surface, whereas it depends on the gradient of concentration in the diffusion layer whether the electrode can be made passive. The before described phenomenon that not always the most negative electrode is most difficult to passivate, is in agreement with this.

So far the phenomena can, therefore, be explained by the aid of the hydrogen theory. That the phenomena are caused by a particular state of the metal surface, and not of the liquid, appears from this that they qualitatively remain the same, when the liquid is vigorously stirred, and also when the liquid is entirely renewed. The potential of the electrode only becomes *somewhat* more positive by stirring. This is probably owing to this, that in consequence of the stirring the solution contains more oxygen, and the hydrogen is more quickly withdrawn from the chromium surface. When the stirrer is stopped, the potential falls again.

In these experiments the chromium anode was placed in a saturate solution of KCl, the cathode in a same solution in a porous vessel. This latter liquid became alcalic during passage of the current. The solution round the anode became on the other hand *acid*. To determine the degree of acidity a hydrogen electrode was placed in this solution. It presented a potential —0.58 V. with respect to the n. calomel electrode, corresponding with a hydrogen ion concentration of 10^{-5}. A current of 4 mA had been led through this solution for 20 hours.

That the solution became acid can be explained by a hydrolytic splitting up of the formed $CrCl_2$, or by the hydrogen present in the chromium going anodically into solution as H.

As the volume of the solution amounted to about 300 cm^3, and

the hydrogen ion concentration was 10^{-5}, there has been formed 0.003 mgr. aeq. of hydrogen ions, 3 mF having gone through the solution. Hence the chromium would have to contain 0.1 % hydrogen in order to give the above mentioned degree of acidity to the solution. In reality this must be slightly more, because part of the OH ions has moved from the cathode space to the anode space, and has, therefore, partly neutralized the acid formed.

It also appeared in these experiments that the potential which the chromium electrode presents, is really a chromium potential, or at least no hydrogen potential. In the acid solution the potential was namely —0.59 V. When the solution was then made feebly alcalic, the potential rose to —0.58 V, whereas a hydrogen electrode in the same liquids would have to present a decrease of about 0.2 V. In this and in other experiments the chromium developed hydrogen. This cannot be hydrogen that the chromium developed spontaneously from the liquid, for in this case the potential of the chromium electrode would have to be more negative than that of a hydrogen electrode in the same liquid. This was not the case here; the potential of the hydrogen electrode was —0.58, that of the chromium electrode —0.52. Besides the hydrogen generation took just as well place in a feebly alcalic solution as in a feebly acid solution, whereas the potential of the chromium electrode was often pretty much more positive than —0.52 V. It is possible that the chromium contains more hydrogen than dissolves anodically, and that part of it escapes in gaseous form.

Hence it must be assumed that the examined chromium always contained hydrogen. In the case of electrolytic chromium this has been separated at the same time with the chromium in a considerable quantity, whereas the chromium of GOLDSCHMIDT contains a slight quantity. By treatment with molten KCl + NaCl or $ZnCl_2$ the chromium can absorb more hydrogen in consequence of the decomposition of the water present in it by the chromium. On the action of chromium on these molten salts development of a combustible gas and formation of chromium oxide was always observed. That $ZnCl_2$ activates more strongly than KCl + NaCl could be explained by this, that the hygroscopic $ZnCl_2$ contained more water, and can, therefore, yield more hydrogen. The activity which chromium obtains by treatment with hydrochloric acid and by increase of temperature must, however, chiefly or exclusively be attributed to the hydrogen which is naturally present in the metal.

With regard to the hydrogen generation at chromium during the anodic polarization it should still be pointed out that this ceases

after the polarizing current has been broken for some time, and in general is the weaker as the strength of the current is the smaller. This hydrogen generation is, however, in no connection with the other phenomena on anodic polarization, as the hydrogen generation failed to appear in a number of experiments, though the anodic behaviour was the same for the rest.

The explanation of the phenomena on cathodic polarization presents one difficulty, viz. that through the cathodically separated hydrogen, the metal in a solution of KCl is not activated. The metal, indeed, gets a strongly negative potential, but the strength of the current which the chromium anodically can bear, is not greater than before the cathodic polarization. To explain this it should be assumed that the cathodically developed hydrogen only remains at the metal surface, and does not diffuse, or only very slightly, into the metal.

Amsterdam, March 1918. *Chemical Laboratory of the University.*

Physiology. — *"On the influence of the increase of the osmotic pressure of the fluids of the body on different cell-substrata."* By Dr. S. DE BOER. (Communicated by Prof. G. VAN RIJNBERK).

(Communicated in the meeting of March 23, 1918.)

In the following experiments an investigation was made into the influence of the increase of the osmotic pressure of the fluids of the body on the vital functions of frogs. The increase of the osmotic pressure was brought about along different ways, which I intend to indicate here successively, mentioning at the same time the phenomena I observed.

I. Frogs were placed into a hyperisotonic solution of RINGER containing instead of 6.5 gr. (p. L.) NaCl 18 gr. NaCl. Such a quantity of this fluid was poured into the vessel in which the frogs had been removed, that the head and the back projected above it. A considerable part of the surface of the skin was then in contact with the hyperisotonic solution of RINGER. When the frogs had remained in this solution for about 20 hours, they showed a series of phenomena as a consequence of the increase of the osmotic pressure of the fluids of the body. The first phenomenon that is observed, is the comatous condition. The frog sits still in a squatting position with the connective fleeces (membranes) before the eyes, and no longer leaps about. If one stretches out a hindleg, this abnormal posture of the leg is indeed corrected again but very sluggishly. After a longer residence in the hyperisotonic surroundings this correction does not take place. Irritations of the skin have a slight reflectoric effect which in a later stage is likewise reduced to

Fig. 1.

a minimum. The muscles show a strong inclination to contractions.

At the same time the respiration shows a periodicity that is known by the name of Cheijne-Stokes' respiration. Groups of dyspnoea alternate here with pauses. In Fig. 1 we see curves of this phenomenon which were registered by suspension of the skin in one of the flanks. During the flank-movements the pharyngeal respiration continued likewise and in such a manner that after each flank-movement a movement of the mouth-bottom could be observed. In the pauses both these movements ceased.

The curves of Fig. 2 were registered with another frog by placing a cork cylinder through which a pin had been pierced, on the back. The up-and downward movements of this cylinder were enlarged by a lever-system and registered on a drum covered by smoked

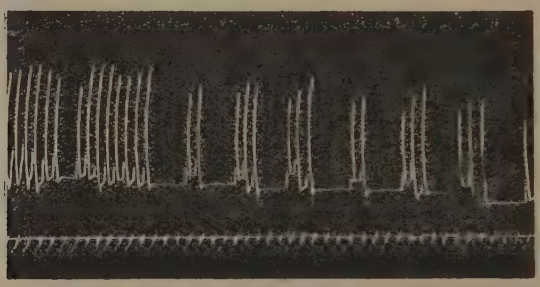

Fig. 2.

paper. The flank-movements were here likewise accompanied by movements of the mouth-bottom, whilst in the pauses both these movements ceased. In both figures we see in the beginning of the groups the ascending degree indicated. The periodic respiration was succeeded by a cessation of the respiration. This cessation was reached, after the animal had remained about 24 to 25 hours in the hyperisotonic solution of RINGER.

I found likewise a constantly occurring deviation at the eye-lenses. The surface of the pupil had the appearance of *cataract.*

The phenomena enumerated above were caused by the increase of the osmotic pressure of the liquids of the body. A few more controling experiments were made in this respect.

Whilst the periodical respiration was still going on, or likewise whilst a cessation of the respiration had already set in, the frog was put into the water. After the animal had been in the water for 24 hours, all the phenomena mentioned above had disappeared. The frog was then again quite normal, the passivity, the reflectionlessness and coma had entirely disappeared. The respiration was then again normal,

the cataract had entirely or almost entirely disappeared. (After the frog had remained in water for 2 days not a vestige of the cataract was left). The frog could not in any respect be distinguished from a normal one.

A second controlexperiment was made in the following manner: The frog was put in the hyperisotonic solution of RINGER, and at the same time a canule was fastened in the dorsal lymph-bag. Slowly water was poured into the lymph-bag through this canule. Under these circumstances the fluids of the body did not become hyperisotonic, as the water that was withdrawn from the frog along the skin, was replaced again along the lymph-bag. In this way the frogs could remain alive during a week without showing the above mentioned symptoms. Without the drainage of the lymph-dorsal-bag the frog dies in the hyperisotonic solution of RINGER within one day and a half.

II. Instead of the hyperisotonic solution of RINGER a hyperisotonic solution of glucose was used (1.38% solution). The frogs behaved in this solution in exactly the same manner.

III. In a third series of experiments fluid was withdrawn from the frogs by placing them in a dry bottle, and sucking through the latter by means of a water-jet-suctionpump air that had previously passed through lime-tubes. After one day and a half such a frog had desiccated so much as to show the same symptoms as a frog that had been placed in a hyperisotonic fluid. After it had been removed into the water again a complete restoration set in likewise.

IV. In a fourth series of experiments the blood was replaced from the vena abdominalis by a hyperisotonic solution of RINGER (with 18 gr. NaCl per L.). When the fluid had streamed through the frog for 15 to 20 minutes, the same phenomena of coma, passivity and reactionlessness set in. The respiration was then periodical (Cheyne-Stokes' respiration) or stopped entirely. In the latter case the Cheyne-Stokes' respiration could be restored by placing the frog for a short time into water. A beginning of cataract could already be observed, when the drainage had lasted 15 to 20 minutes. If no further measures were taken, the cataract augmented considerably after the drainage in the course of 10 to 15 minutes.

All phenomena disappeared likewise in this series of experiments when the frog was removed to water.

A short description of an experiment may follow here.

$11^1/_2$ o'clock. From the vena abdominalis a frog is drained with a hyperisotonic solution of RINGER during 25 minutes. Coma, passivity

cessation of the respiration, when it is turned on its back, the frog does not move, abnormal position of the leg is not corrected, cataract of both the eyes [1]).

Fig 3.

At 1 o'clock placed in water.

1½ o'clock. The frog shows now and then a respiration.

2 o'clock Cheyne-Stokes' respirations.

Whilst the frog continues to lie on its back in the bottle of water, the number of respirations per group and the duration of the pauses during some time are registered.

Here follows the result:

9 respirations	58 sec. pause
1 minute pause	14 respirations
9 respirations	62 sec. pause
½ minute pause	11 respirations
5 respirations	45 sec. pause
40 sec. pause	13 respirations
11 respirations	40 sec. pause
70 sec. pause	20 respirations
11 respirations	62 sec. pause

This observation has this advantage over the registration, because on account of the suspension the respiration of the frog varies temporally at least often.

After this the respiratory curves were registered by suspension of the mouth-bottom, as LANGENDORFF did for the first time. The first 8 minutes after the suspension the respiration stopped entirely. Thereupon the groups reappeared again. Fig. 3 represents some of these. The bottom row was registered ½ hour, the top one 10 minutes after the suspension.

When we compare the respiratory-curves of these groups with the curves

[1]) In order to control the experiment the two lenses were extirpated after the experiment and compared with normal extirpated lenses. The latter were clear and transparent, the former turbid and opalescent.

of the normal respiration, it appears that with each movement of the mouth-bottom one movement of the flanks takes place during these groups.

Only the two first groups of the top-row set in with a separate expiration-movement, which is not followed by a movement of the mouth-bottom. For the rest all groups begin with an expiration, as appears from the fact that the lever descends in the beginning. During the normal respiration the frogs show one flank-movement with some movements of the mouth-bottom. During the groups of the Cheyne-Stokes' respiration every movement of the mouth-bottom is almost always followed by one flank-movement. In this way the frog respires likewise when it is dyspnoeic.

If the blood of frogs is replaced by normal isotonic solution of RINGER instead of hyperisotonic fluid of RINGER the mentioned phenomena do not occur. The respiration remains normal, the lense does not become turpid.

A more explicit discussion of the cataract and the Cheyne-Stokes' respiration follows here.

Cataract.

In whatever way the fluids of the body of frogs may be made hyperisotonic, cataract occurs always. *The cataract disappears however again, when the osmotic pressure of the fluids of the body is made normal again.*

The cataract develops itself very slowly. When after a perfusion during 15 or 20 minutes the respiration has stopped already, the surface of the pupil begins only to become a little dim. If then one waits a short time without continuing to drain the circulation-apparatus, the dimness gradually increases. At last two vertical parallel white stripes are observed on the lense, between which there is a long dark stripe. It makes the impression as if one sees two white walls and between these a deep, dark moat. The direction is usually vertical, sometimes almost vertical. This vertical stripe will correspond to the frontal vertical suture of the lens, as it is described in GAUPP. (Anatomie des Frosches). One often sees white, thin lines proceeding in a radiary direction from this vertical line, corresponding to the so-called spokes of the human cataract. It is obvious that the origin of the cataract must be attributed to a congelation of the albuminous substances in consequence of an increase of the saltconcentration of the fluids of the body. As soon as the osmotic pressure of the fluids of the body decreases again, the process is likewise converted. In my opinion another explanation of the phenomenon is impossible.

It is obvious that also every other circumstance by which a congelation of albuminous substances is caused, can bring about lense-cataract. In my opinion however it is of importance that I have indicated, that a mere increase of the osmotic pressure of the fluids of the body can result in cataract.

Cheyne-Stokes' respiration.

The periodical respiration was caused in my experiments by an increase of the osmotic pressure of the fluids of the body. The periodical respiration disappeared likewise again as soon as this pressure did not exist any longer. In order to study the origin of the Cheyne-Stokes' respiration more accurately the desiccation of the frogs was continued in a series of experiments so far, that the Cheyne-Stokes' respiration had not yet set in. Thereupon the mouth-bottom was suspended and in a warm room the frog was exposed to further desiccation. Usually the Cheyne-Stokes' respiration slowly set in there in the course of a few hours. During these experiments it appeared that besides a periodicity of the flank-respiration we must distinguish a periodicity of the pharyngeal respiration. In far advanced stages the two periodicities coincide, so that then during the groups movements of both the flanks and the mouth-bottom take place, whilst in the pauses the respiration stops entirely. As a transition to this complete Cheyne-Stokes' respiration we find a stage in which the groups are equal to those of the complete Cheyne-Stoke's respiration, but during this stage the movements of the mouth-bottom continue. It appears consequently that both ways of respiration are to a certain degree independent of each other, as appears indeed also from the normal respiratory curves.

According to the examinations of LANGENDORFF the movement of the flanks comes off passively without a contraction of the pectoral muscles. If this is correct, then the movement of the flanks is after all made possible by an active opening of the glottis. With the Cheyne-Stokes' respiration the periodicity of the movement of the flanks is determined by a periodicity of the glottis-muscles. An opening of the glottis is almost constantly followed by a movement of the mouth-bottom, this however is not necessary either. The first 2 groups of Fig. 3 set in with an expiration that is brought about by an opening of the glottis, which is however not followed by a movement of the mouth-bottom.

One word more about the cause of the Cheyne-Stokes' respiration in these experiments. As I explained already, this phenomenon

occurs at a hyperisotony of the fluids of the body. This hyperisotony leads in the end to a cessation of the respiration. Like the cataract this cessation of the respiration can be suppressed again by a decrease of the osmotic pressure. Consequently the setting in of the cessation of the respiration in hyperisotonic surroundings, just as the Cheyne-Stokes' respiration that precedes it, and likewise the development of cataract originate in modifications that are reversible.

Chemistry. — *"On the Electrochemical Behaviour of Metals"*. By Prof. A. SMITS. (Communicated by Prof. ZEEMAN).

(Communicated in the meeting of March 23, 1918).

1. *Introduction.*

By application of the considerations on which the theory of allotropy is based to the internal state of the metals and to their chemical as well as to their electromotive behaviour, we are enabled to consider all the metals, also those which serve as so-called unattackable electrodes, from the same point of view.

These considerations rest on the more than probable assumption that every metal contains metal atoms, one or more kinds of metal ions, and electrons, which can be in equilibrium under definite circumstances. When a metal is immersed in an electrolyte, then in agreement with NERNST's views of the phenomenon of solution, the heterogeneous equilibrium between the metal and the boundary layer will be established with so great velocity, that it may be said that this equilibrium always exists.

When we, therefore, restrict ourselves to the simple case that the metal consists of metal atoms, v-valent ions, and electrons, we may say, that when this metal is immersed in an electrolyte the following heterogeneous equilibria will at once set in.

$$\begin{array}{ccc} M_s & M_s{}^{v\cdot} & v\theta_s \\ \downarrow\uparrow & \downarrow\uparrow & \downarrow\uparrow \\ M_L & M_L{}^{v\cdot} & v\theta_L \end{array}$$

Whether the homogeneous equilibrium will also exist in the two coexisting phases between the metal atoms, metal ions, and the electrons, depends on different circumstances. Whereas it seems that a metal in perfectly dry condition can assume internal equilibrium as a rule only at comparatively high temperature, this often takes place very quickly when in contact with an electrolyte, but it may also occur that the metal gets in equilibrium very slowly, or not at all, under these circumstances at the ordinary temperature.

The velocity with which a metal assumes internal equilibrium under definite circumstances is undoubtedly one of the most characteristic properties of the metal.

2. *The Potential Difference Metal-Electrolyte when the Metal is Attacked.*

When a metal in contact with an electrolyte superficially assumes internal equilibrium with very great velocity, the internal state in the metal surface remains unchanged, in whatever way the metal may be attacked.

Let us suppose that we immerse zinc in an aqueous solution of hydrochloric acid; then hydrogen generation takes place, because the electron concentration of the metal equilibrium

$$Zn_L \rightleftarrows \ddot{Zn}_L + 2\theta_L \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in the solution is greater than the electron-concentration of the hydrogen equilibrium:

$$H_{2L} \rightleftarrows 2\dot{H}_L + 2\theta_L \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Hence the electrons of the equilibrium (1) are removed, and through this the equilibrium is disturbed. It is now the question how the equilibrium can be restored.

The concentration of the zinc-atoms in the liquid is so small that even if the reaction constant of the conversion

$$Zn_L \rightarrow \ddot{Zn}_L + 2\theta_L$$

was very large, yet only exceedingly few zinc ions and electrons would be split off per second in this way.

The only way in which the state of equilibrium can be restored is this that the metal sends electrons into solution, which is of course accompanied by zinc ions going into solution, because zinc-ions and electrons, with a difference of only a very small amount, are always present in the same concentration.

Through this process the internal equilibrium in the metal surface is disturbed, which can be restored again by the reaction:

$$Zn_s \rightarrow \ddot{Zn}_s + 2\theta_s \, .$$

As the heterogeneous equilibrium in the boundary layer sets in with very great velocity, the question whether the metal zinc during solution in an acid will be disturbed, comes to this, whether the internal equilibrium in the surface of the metal sets in with so great velocity that the concentration remains practically unchanged.

This is actually the case for zinc under certain circumstances. Mr. Hüffer S. J., who examined some metals at my request, found among others, that when the potential difference between zinc and a solution of zinc-chloride is measured during vigorous stirring, and then that between zinc and a zinc-chloride solution of the same

concentration acidified with hydrochloric acid, *the potential difference retains the same value, notwithstanding a strong hydrogen-generation takes place in the latter case.*

The metal zinc is, therefore, not disturbed through solution in hydrochloric acid, and this result is in perfect agreement with what is found when zinc is anodically brought to solution in a zinc-chloride solution. In this process, which likewise rests on the withdrawal of electrons from the metal, the potential difference, zinc-electrolyte, does not change appreciably, even for comparatively great densities of current, so that our investigations about the potential difference *during* the solution of zinc in a hydrochloric acid solution, as well as the measurements of the potential difference of the same metal on anodic solution in a solution of zinc-chloride lead to the result that the equilibrium in the metal zinc in contact with the above-mentioned electrolyte sets in with a velocity which is very great compared with the velocity with which electrons and ions are withdrawn from the metal.

3. *General consideration.*

When we now consider the phenomenon in general, we can distinguish the following cases.

On immersion of a metal in an acid we have in the simplest case among others the two following equilibria in the electrolyte:

$$H_{2_L} \rightleftarrows 2H_L + 2\theta_L.$$

and

$$M_L \rightleftarrows \dot{M}_L + \theta_L$$

The electron-concentrations of these two equilibria are in general different, and a consequence of this is that either the electrons of the metal equilibrium, in the liquid, combine with the hydrogen ions of the hydrogen equilibrium, which causes electrons + ions from the metal to go into solution, or the electrons of the hydrogen equilibrium with the metal ions of the metal equilibrium pass from the electrolyte into the metal.

Let us first imagine the limiting case, viz. this that the internal equilibrium of the metal surface is established with great velocity, so that this velocity is very great with respect to the velocity with which electrons + ions are withdrawn from the metal or are added to the metal, then the metal surface will not change independent of whether one process takes place or the other, and the potential

difference metal-electrolyte will remain equal to the potential difference of the unary metal.

In the second place the case may present itself that the internal equilibrium of the metal surface does not set in so rapidly as was supposed above, and then it will be possible to disturb the metal surface either in one direction or in the other, i.e. it may become either nobler or baser, hence the potential difference can differ from that of the unary metal in noble or base direction.

A third case, which like the first, represents a limiting case, is this that the metal is so inert that the velocity with which it assumes internal equilibrium is very small compared with the velocity with which the electrons and ions are withdrawn from the metal or added to it.

In the first limiting case the potential difference is entirely governed by the state of internal equilibrium of the metal, and in the last case the potential difference is dominated by the electron concentration of the hydrogen equilibrium in the electrolyte.

4. *Nickel as Example of an Inert Metal, the Inertia of which Increases under the Influence of the Dissolved Hydrogen.*

An example of the latter case with this particularity, however, that the just mentioned great inertia is only slowly reached, because the metal is converted to this state after some time through the negative catalytic influence of the dissolving hydrogen, is furnished by nickel. As was shown in a previous communication, the case presents itself that when this metal is immersed in such an acid solution that hydrogen generation would have to take place, this phenomenon does not take place to an appreciable degree, and the metal appears to be disturbed after some time so far in a noble direction that its potential difference has become equal to that of the hydrogen electrode.

On that occasion we already gave an explanation of this phenomenon, and pointed out that, nickel being so inert, the electron concentration of the nickel equilibrium in the electrolyte

$$Ni_L \rightleftarrows Ni_L^{\cdot\cdot} + 2\theta_L$$

becomes equal to the electron concentration of the hydrogen equilibrium:

$$H_2 \rightleftarrows 2H^{\cdot} + 2\theta$$

so that finally

$$(\theta_{Ni})_L = (\theta_{H_2})_L .$$

This was demonstrated in the following way. We pointed out

namely, that on application of the electron equation for the potential difference, metal-electrolyte, for the derivation of the relation for the electromotive force of a circuit consisting of two metals immersed in the corresponding salt-solutions, we arrive at the following equation:

$$\Delta_1 - \Delta_2 = \frac{\mu_{\theta_{s_1}} - \mu_{\theta_{s_2}}}{F} - \frac{RT}{F} ln \frac{(\theta_{L_1})}{(\theta_{L_2})}.$$

so that, taking into consideration, that the first term of the second member denotes the Volta-effect of the two metals, which is a very small quantity, the electromotive force $\Delta_1 - \Delta_2$ will be zero in first approximation, when $(\theta_{L_1}) = (\theta_{L_2})$.

In the case discussed here the metals 1 and 2 are nickel and hydrogen, and experiment has taught that $\Delta_{Ni} - \Delta_{H_2}$ was really practically zero, from which therefore followed $(\theta_{Ni})_L = (\theta_{H_2})_L$.

Through the inertia of the metal nickel, which inertia was still increased by the hydrogen dissolved in the metal, which is here a negative catalyst, as was already stated before, the metal could, therefore, be disturbed so far, that the electron concentration of the nickel equilibrium in the electrolyte had become equal to the electron-concentration of the hydrogen.

We may, therefore, also express ourselves in a different way, and say, that the nickel had been passivated by the acid. Finally the nickel phase and the hydrogen phase present the same potential difference, accordingly these phases, which are in contact with the same electrolyte, can coexist. As in the case discussed here the nickel will of course be covered by a layer of hydrogen, the found potential difference refers to the three-phase equilibrium Ni + H_2 + + electrolyte.

5. *Unattackable Electrodes.*

As follows from the communication cited here, this disturbance is comparatively slowly reached for nickel. There are, however, metals for which this goes much quicker, and these are the metals of which the so-called unattackable electrodes consist, as the platinum metals.

These metals belong to the group of the most inert metals that we know. Even in contact with an electrolyte these metals do not get in internal equilibrium, but they are almost always in passive state, so that the potential difference of the unary metal is not even known to us.

When such a metal is immersed in a solution of HCl or H_2SO_4,

and hydrogen is passed through, the electron concentration of the platinum equilibrium in the electrolyte

$$Pt_L \rightleftarrows \overset{\cdot\cdot\cdot\cdot}{Pt_L} + 4\theta_L$$

has almost immediately become equal to the electron concentration of the hydrogen equilibrium,

$$H_{2_L} \rightleftarrows 2\dot{H}_L + 2\theta_L$$

corresponding to the pressure of the hydrogen that passes through, so that e. g. the platinum electrode has almost immediately become electromotively equal to the hydrogen electrode.

For these metals, which behave *ideally inert*, the potential difference is, therefore, governed by the existing electron concentration in the electrolyte. This is also the reason why these exceedingly inert metals may serve not only as gas-electrodes, but also for the determination of the so-called oxidation, resp. reduction potentials.

When e. g. platinum is immersed in a solution in which the equilibrium:

$$\overset{\cdot\cdot}{Fe}_L \rightleftarrows \overset{\cdot\cdot\cdot}{Fe}_L + \theta_L$$

prevails, the electron concentration of the platinum equilibrium in the solution has almost immediately become equal to the electron concentration of the above ferro-ferri equilibrium, so that in the electron equation for the potential difference of the platinum

$$\Delta = \frac{RT}{F} ln \frac{K_\theta}{(\theta_L)}$$

the electron concentration of the ferro-ferri equilibrium may be written instead of (θ_L), in consequence of which we get:

$$\Delta = \frac{RT}{F} ln \frac{K_\theta}{K} \frac{(\ddot{Fe})}{(\overset{\cdot\cdot\cdot}{Fe})},$$

as was already stated before.

The peculiar feature of these platinum metals is therefore their extraordinary inertia, which causes them to behave ideally passive in most electrolytes.

6. *Considerations in the Light of the Theory of Phases.*

It is clear that for the explanation of the phenomena discussed here, considerations as have been introduced by us of late, are indispensable.

Phase-theoretical considerations are inadequate here, but all the same it may be of use to represent the obtained results graphically by means of Δ,x-diagrams.

Let us first consider the case that the metal zinc is immersed in a hydrochloric acid solution of $ZnCl_2$; then it is the Δ-x-figure of the system Zn-H_2 that may serve for the graphical elucidation of the found result.

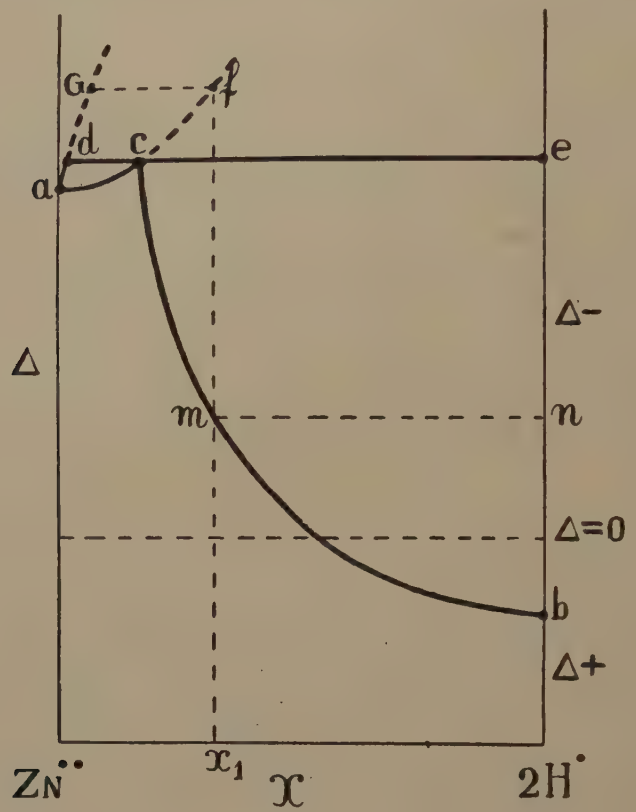

Fig. 1.

Zinc.

A Δ-x-figure holds for constant T, P, and a constant total ion-concentration; for T we choose here the ordinary temperature, and for P the pressure of 1 atm., the total ion-concentration being put here at 2 norm.

The situation of the point C, which represents the electrolyte which coexists with the zinc phase and the hydrogen phase of the pressure of 1 atm., is found from the equation:

$$\frac{RT}{2F} ln \frac{K_{Z\ddot{n}}}{(Z\ddot{n}_L)} = \frac{RT}{F} ln \frac{K_{H}}{(\dot{H}_L)}$$

from which follows:

$$\frac{K_{Z\ddot{n}}}{K_{\dot{H}}} = \frac{(Zn_L)}{(\dot{H}_L)^2}$$

or also from the equations for the product of solubility of zinc and hydrogen:

$$L_{Zn} = (\ddot{Zn})\,(\theta)^2$$

and

$$L_{H_2} = (\dot{H})^2\,(\theta)^2$$

by putting $(\theta)_{Zn} = (\theta_{H_2})$, in consequence of which:

$$\frac{L_{Zn}}{L_{H_2}} = \frac{(\ddot{Zn}_L)}{(\dot{H}_L)^2}$$

or

$$\frac{(\ddot{Zn}_L)}{(\dot{H}_L)^2} = \frac{10^{2\times-35}}{10^{2\times-48}} = 10^{26}.$$

When we put for a moment $(\ddot{Zn}_L) = 1$, then:

$$(\dot{H}_L) = 10^{-13}.$$

We see therefore, that the point C lies so much on one side that practically it coincides with the zinc-axis. Hence the line d, c, e or the line for the three-phase equilibrium zinc-hydrogen-electrolyte lies practically on the same level as the point a, so that the measured potential difference of the zinc, which contains a little dissolved hydrogen, and is besides covered with a layer of hydrogen, is certainly practically equal to the potential difference of the pure hydrogen-free zinc, the measurement of which is impossible here.

Let us now suppose that we immerse zinc in an electrolyte, the composition of which, as regards the zinc- and hydrogen ions, is x_1; we then see, that zinc *cannot* be in stable electromotive equilibrium with this liquid, but that hydrogen can.

If, however, the hydrogen did not appear as a new phase, but only dissolved in the zinc, a metastable electromotive equilibrium would, indeed, be possible, viz. g f, but the potential difference would be more strongly negative than that of the three-phase equilibrium represented by the line d, c, e.

This metastable electromotive equilibrium does not appear, however; on the contrary, we observe a generation of hydrogen, and we will point out here in a few words, how the experimental fact is to be explained that under these circumstances the potential difference zinc-electrolyte is equal to that which corresponds with d, c, e, or what is practically the same thing, with a.

The explanation is this: when zinc is immersed in the electrolyte of the concentration x_1, the establishment of the three-phase equilibrium between the zinc phase, the electrolytes, and the hydrogen phase takes immediately place in the boundary layer.

Accordingly the concentration c prevails in the boundary layer, whereas the total concentration of the electrolyte is x_1.

The hydrogen ions now diffuse in the boundary layer, where for the maintenance of the concentration c the reaction:

$$2H^{\cdot} + 2\theta \rightarrow H_2$$

takes place, in consequence of which, as we have already seen, electrons and zinc ions from the metal phase go into solution. The zinc phase assumes internal equilibrium with great velocity, and consequently it remains unaltered during the hydrogen generation, and the measured potential difference is that of the three-phase equilibrium d, c, e, which practically agrees with that of pure zinc, a.

When a platinum electrode is placed in the same electrolyte, it indicates the hydrogen-potential which corresponds with the line $m\ n$. The zinc electrode and the hydrogen electrode present therefore entirely different potential differences in the same electrolyte.

This is the graphical elucidation for our conclusion that the potential difference of zinc with respect to a solution of $ZnCl_2$ acidified with hydrochloric acid is determined by the state of internal equilibrium of the zinc.

Nickel.

Let us now proceed to the case that instead of zinc the metal nickel is taken; then it is worthy of note in the first place that under the same circumstances we then find for the composition of the electrolyte c

$$\frac{K_{Ni^{\cdot\cdot}}}{K_{H^{\cdot}}} = \frac{L_{Ni}}{L_{H_2}} = \frac{(Ni^{\cdot\cdot}_L)}{(H^{\cdot})^2} = \frac{10^{2\times-45}}{10^{2\times-48}} = 10^6$$

When we now put $(Ni^{\cdot\cdot}_L) = 1$, we get $(H^{\cdot})^2 = 10^{-6}$ or $(H^{\cdot}) = 10^{-3}$.

Here, too, the electrolyte c has still a one-sided position. Let us assume that the adjoined figure 2 again holds for 18°, and a pressure of 1 atm. for a total-ion concentration of 2-norm.; then an entirely different phenomenon is observed on immersion of a nickel-electrode in the electrolyte of the concentration x_1 than in the case with *zinc* discussed just now, because the internal equilibrium in the metal surface cannot maintain itself when electrons and nickel ions go into solution.

The metal is more and more disturbed in noble direction, and the result is, as we demonstrated already, that the electron-concentration of the nickel equilibrium in the solution has become equal to the electron-concentration of the hydrogen-equilibrium in the electrolyte,

in which the potential difference of the nickel electrode has become equal to that of the hydrogen electrode. This may be graphically represented in the way as has been done in fig. 2.

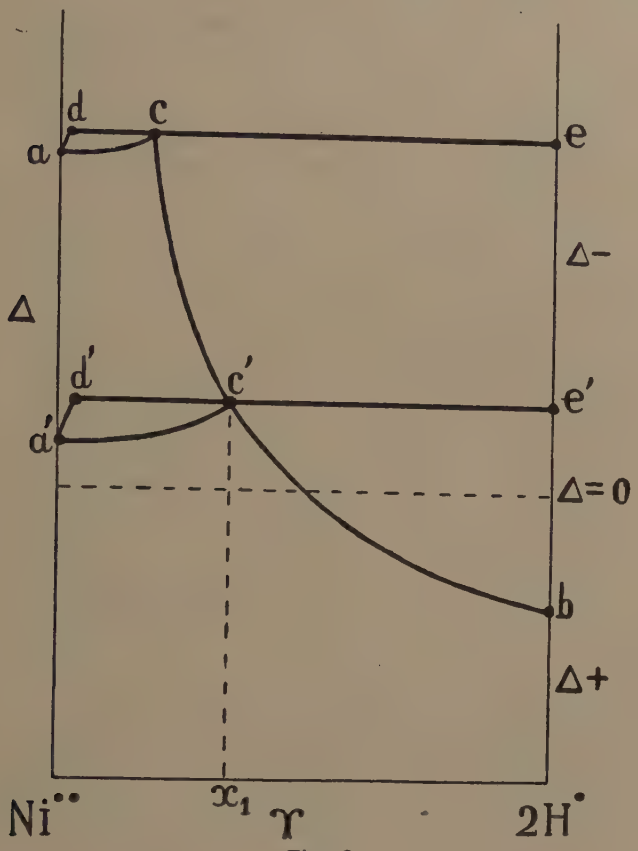

Fig. 2.

In consequence of the disturbance point d has got in point d', and represents, therefore, the ennobled nickel phase which coexists with c' and the hydrogen phase e'.

It could be derived from our considerations how we have to proceed when we want to know the potential of the unary nickel, or in other words the equilibrium-potential. Then the nickel is to be brought into a solution with a hydrogen-ion-concentration, smaller than that in the electrolyte c. Then our Δ, X-diagram 3 shows that under these circumstances e.g. the electromotive equilibrium between the nickel phase d'' and the electrolyte c'' will be established, the potential difference of which practically coincides with that of the unary metal, which is perfectly free from hydrogen and indicated by a.

It is necessary to point out that when a metal is in electromotive equilibrium with a coexisting electrolyte, the electron-concentration

of the metal equilibrium must always be equal to the electron-concentration which exists in the liquid in consequence of the other prevailing equilibria.

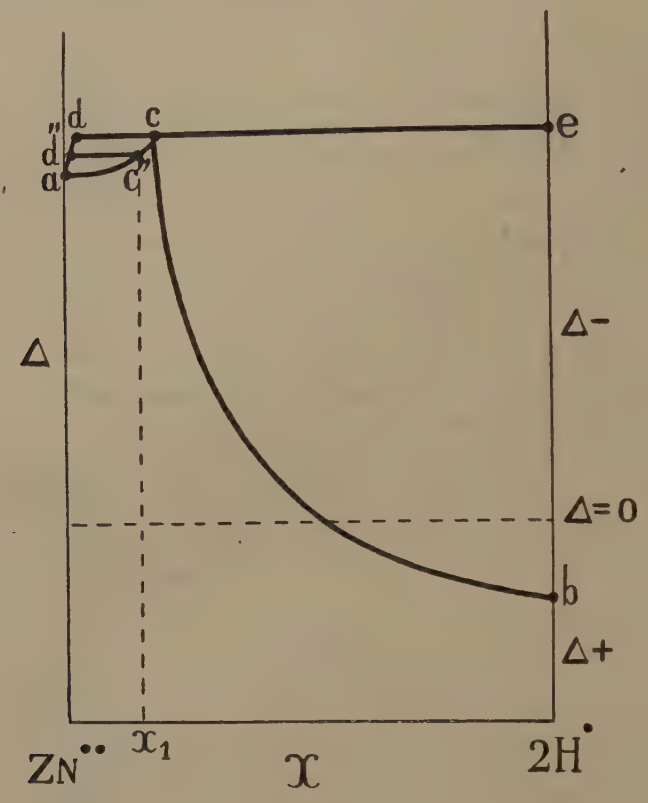

Fig. 3.

In this case we may say, that the metal is really in equilibrium with the electrolyte. When the metal dissolves in an acid, or when a metal is deposited, the just mentioned equality of electron-concentration prevails only in the boundary layer between metal and electrolyte, and diffusion takes continually place in the boundary layer.

The just mentioned equality of the indicated electron-concentrations must, therefore, also exist when in the case mentioned just now the metal nickel has got in equilibrium with the electrolyte. Of course there are always some transformations required for this, but these are soon over, and can, therefore, not give rise to a permanent disturbance, at least if the solution has been freed as much as possible from air and hydrogen by boiling in vacuum.

We have acted upon this principle, and, as was communicated in the preceding paper by Mr. Lobry de Bruin and myself, by this procedure the equilibrium-potential was found of nickel that contained

only a trace of hydrogen, so that the found potential difference will practically very certainly agree with that of the purely unary metal.

It is supposed here that the potential difference between nickel and the nickelsalt solution with the exceedingly small hydrogen-ion-concentration, is measured after the electrolyte has been heated with the nickel electrode in vacuum, after the whole apparatus has been

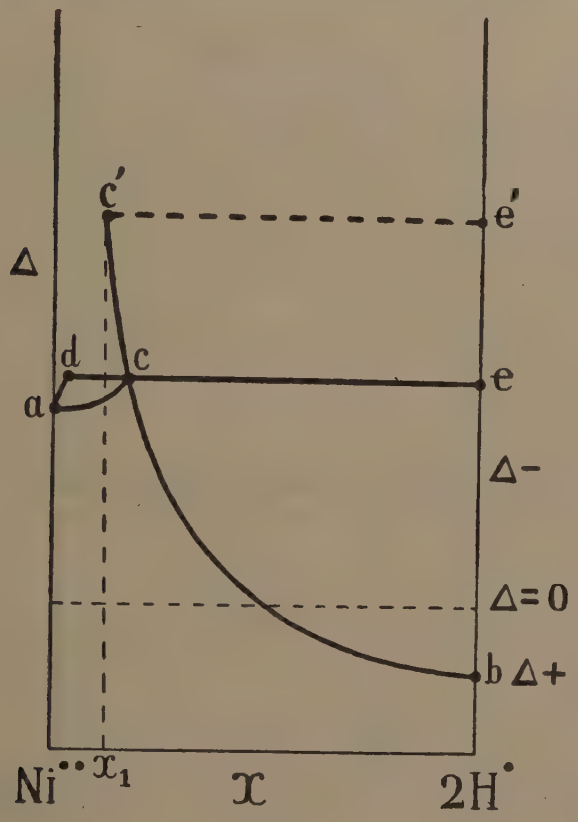

Fig. 4.

filled with the electrolyte and connected with the 1 N. Calomel electrode by means of a siphon and a liquid circuit, so that the pressure under which the electrolyte is, amounts to 1 atm. also in this case.

An entirely different result is obtained when the foregoing measurement does not take place in vacuum, but in a hydrogen current.

In this case the nickel electrode is disturbed, but the disturbance does not take place now in a noble direction, but in a base direction, and as we showed before the potential difference of the nickel has again become equal to that of the hydrogen-electrode. This result can again be brought to expression in an exceedingly simple way by means of a Δ, X-fig. 4.

When we lead hydrogen through the electrolyte, of which the concentration x_1 lies on the lefthand of the point c, the potential of he hydrogen-electrode is indicated by the line $c'\,e'$. In this mode of procedure the nickel electrode gets in contact with gaseous hydrogen, and in the boundary layer which is simultaneously in contact with nickel and hydrogen, the electrolyte c will be formed in consequence of the reaction:

$$H_{2L} \rightarrow 2\dot{H}_L + 2\theta_L,$$

while electrons and nickel ions (and a few hydrogen ions) are deposited on the metal. This renders the metal baser superficially and both the three-phase equilibrium $d\,c\,e$ and the point a rise.

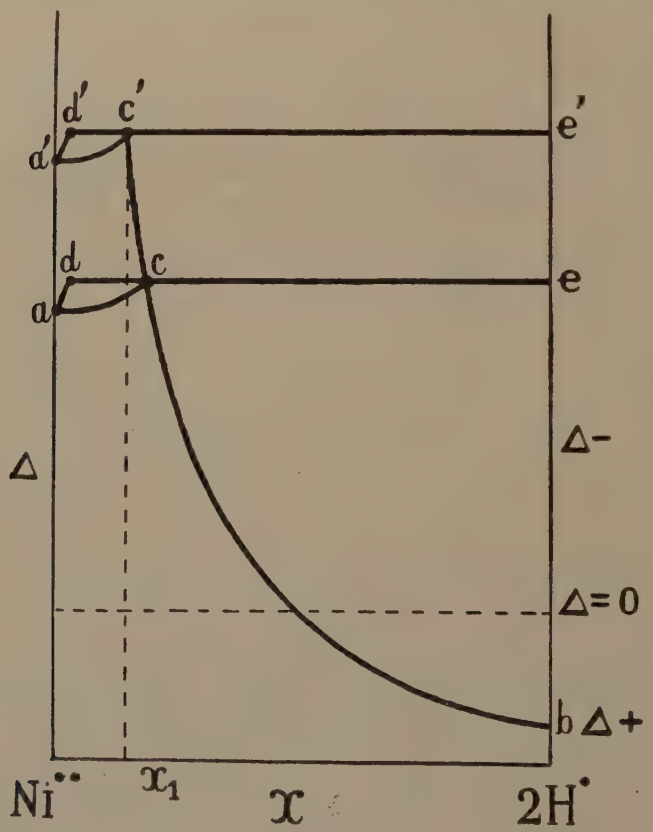

Fig. 5.

This disturbance in base direction continues till the concentration of the electrolyte has become equal to that in the boundary layer. This is the case when a three-phase equilibrium has formed of which the electrolyte possesses the concentration x_1, hence at the place where the curve bc intersects the vertical which corresponds with this concentration. As fig. 5 shows, this takes place in point c'

and the three-phase equilibrium, which therefore finally is established, is here indicated by the points $d' c' e'$. Accordingly also in this case the potential difference of the nickel electrode is equal to that of the hydrogen electrode.

When we now consider the metals of which the unattackable electrodes consist, we need only remark that because as was just now demonstrated, these metals are ideally inert, the potential difference metal-electrolyte is in almost all cases exclusively determined by the electron-concentration in the electrolyte. Hence, when e.g. a platinum electrode is immersed in an electrolyte through which hydrogen is led, the platinum shows the hydrogen potential almost immediately, which was the case for nickel only after some time had passed. When we want to express this graphically in a Δ, X-fig., we get, of course exactly the same representation as for the case nickel-hydrogen.

That in aqueous solutions we cannot determine the equilibrium potential of platinum, whereas this is still possible for nickel is owing to this that the electrolyte c has such an one-sided situation for platinum-hydrogen, that an aqueous solution of a platinum salt always possesses a concentration on the righthand side of the point c as regards the platinum and the hydrogen ions, so that a disturbance must always take place.

In a subsequent communication I hope to enter into a fuller discussion of the phenomenon of the "super-tension", which has already been repeatedly referred to in our considerations without having been named.

Amsterdam, March 1918. *General Anory. Chemical Laboratory of the University.*

Anatomy. — *"On the Nervus Terminalis from man to Amphioxus."* By Prof. J. W. VAN WIJHE. [1])

(Communicated in the meeting of April 26, 1918).

Although hardly credible, it is a fact that a good three years ago — in 1914 — a new nerve, arising independently in the brain, was discovered in man. This is the Nervus Terminalis. Naturally it is not visible to the naked eye, but can be seen through the magnifying glass, especially through the dissecting microscope, with the aid of which its discoverer, the American BROOKOVER found it. (Journ. of Comp. Neurology. Vol. 24.)

It has its course through the pia mater, parallel and mesial to the olfactory bulb and tract, running over the middle of the gyrus rectus (vide fig. 1.) When a rectangular piece of the pia mater in this region is taken up and placed under the microscope, the fine fibres of this nerve can be seen. Here and there the fibres are retracted from each other to come together again later on.

The nerve is independent of the olfactory tract and bulb, and in the opinion of BROOKOVER enters the brain at the mesial root of the tract. A number of ganglionic cells, BROOKOVER taxes their number at about 50, lie spread in the nerve in its course along the olfactory tract.

The nerve can be followed not only along the tract but also somewhat further distally along the olfactory bulb, but in this vicinity it is embedded in the dura mater, while it has here also partially pierced the former and lies on the lamina cribrosa.

In the vicinity of the bulb the number of its ganglionic cells is considerably larger than is the case along the tract. It was estimated by BROOKOVER at about 100 to 200 cells. Undoubtedly its branches pass through the mesial row of openings in the lamina cribrosa to the mucous membrane of the nasal septum, but the research did not extend as far as this.

In adult man the course of the new nerve is as yet known in the brain-case only, not on its outside. [2])

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[1]) Lecture delivered before the meeting of the Neth. Zoological Society, Jan. 26, 1918.

[2]) Vide, however, the postscript at the end of this article.

As was to be expected, in the adults of the mammals the nerve was not first found in man. The dog and the cat (Mc. Cotter. 1913.) and the rabbit (Huber & Guild. 1913.) were the first, but it is remarkable that in the embryonic stages of the mammals the human embryo was the first in which, although incompletely, the nerve was discovered. This was done by our countryman Ernst de Vries, who also observed it in the embryos of the guinea-pig. He described his research (published in the Proceedings of the Royal Academy of Sciences of April the 22nd 1905), which also drew much attention abroad, in an article of four pages, which proves that it is not necessary or even desirable to be loquacious when one has found something of importance.

De Vries found ganglionic cells spread in the course of the nerve which supplies the organon vomeronasale, (the organ of Jacobson, or better the organ of Ruysch) [1]) near the base of the nasal septum. He moreover found that the so-called olfactory ganglion, by him called the ganglion vomeronasale, does not belong to the fila olfactoria, which are taken collectively as the true olfactory nerve. In his opinion it belongs to the N. Vomeronasalis, which supplies Ruysch's organ, lined by a layer divided off from the nasal mucous membrane. As the vomeronasal nerve also enters the central nervous system at a different place — the area vomeronasalis — than do the fila olfactoria, de Vries drew the conclusion that the N. Vomeronasalis is not, as was the general opinion, a component part of the olfactory nerve, but an independent nerve, homologous to the N. Terminalis in the fish.

A serious difficulty to this explanation however is that, according to the illustrations of de Vries, the N. Vomeronasalis issues from the olfactory bulb, while the N. Terminalis of the Dipnoi and the Selachii issues out of the true hemisphere and not out of the bulb. [2])

This difficulty seems to have escaped de Vries's notice. On the first page of his publication he rightly distinguishes between the olfactory lobe and the hemisphere, which are separated from each other laterally by the fissura rhinica, and mesially by the fissura prima. On pages 3 and 4 he states that the area vomeronasalis, where the nerve of this name enters the brain, belongs to the hemisphere. According to his own communication and illustration, however, this area lies at the sulcus circularis bulbi, hence *not* on

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[1]) Concerning Ruysch's organ see postscript at the end of this paper.

[2]) Entering and issuing out of a nerve are used in this address, indiscriminate of the direction in which the impulse moves.

the hemisphere, but on the olfactory lobe. In young embryos the tract is thicker than the bulb, later on this relation is reversed.

It was therefore very desirable that more light were thrown on the question whether the vomeronasal nerve should be considered as the homologue of the N. Terminalis of the fishes.

This happened in 1913 in America, more especially through two publications viz. of JOHNSTON in the Journ. of Comp. Neur. Vol. 23. and of HUBER & GUILD in the Anatomical Record Vol. 7. [1])

JOHNSTON examined embryos of the pig, the sheep, and of man. Besides mammals he also examined embryos of tortoises and a larva of Amblystoma.

The elucidation which JOHNSTON brought, consists herein that (as he found) the ganglion and the ganglionic cells do not belong to the N. Vomeronasalis, but to another nerve, which does not enter the brain in the olfactory bulb, but in the true hemisphere, near or in the lamina terminalis, as is the case in the Selachii.

What DE VRIES had considered as one nerve, was in reality two nerves which for the greater part cover each other; one is the N. Terminalis, the other is the true N. Vomeronasalis.

The vomeronasal nerve has no ganglionic cells and arises out of the cells of a part of the nasal mucous membrane which had been split off (Organon Vomeronasale). In structure and development it is exactly similar to the bundles of the olfactory nerve. It also enters the brain in the olfactory bulb, just as the fila olfactoria, which collectively form the olfactory nerve. It is true that it enters the bulb at a special place, on its mesial plane rising high up caudally, but then it is a *specialised* bundle of the olfactory nerve. The peripheral ganglionic cells and the true ganglion belong to the N. Terminalis.

DE VRIES' mistake is easily comprehensible; he used no special methods to make the nerves visible, could not expose his material of human embryos to this risk and was thus compelled to consider the proximal end of the N. Vomeronasalis (split into four bundles according to him) as a root of the Ganglion Terminale, by him incorrectly called the Ganglion Vomeronasale, which is as it were pasted up against it, while the true roots of this ganglion escape observation in cross section through their fineness. That it is possible to make mistakes even when using nerve-staining methods is proved by the work of DÖLIKEN (1909). He examined embryos of mice, rabbits, guinea-pigs and man. Following in the footsteps of DE VRIES

[1]) Further literature is found mentioned in these publications.

he also took the roots of the N. Vomeronasalis to be those of the N. Terminalis.

Regarding the mouse he says "Die sog. mediale Riechwurzel von der bereits CAJAL, KAPPERS u. A. behauptet haben, sie sei nicht als eigentliche Riechwurzel zu bezeichnen, ist eine Wurzel des N. Terminalis". No wonder that he continues "Sie hat bedeutende Beziehungen zum Olfactorius".

The second important elucidation appeared, as has already been said, in a communication, also in 1913, of HUBER and GUILD, who had come on this subject á propos of the work of JOHNSTON, which had partly been done in HUBER's laboratory.

These writers examined rabbit embryos by the silver-pyridine method. They could fully confirm JOHNSTON's results that the N. Terminalis and the N. Vomeronasalis were two different nerves, and that the ganglion and the disseminated ganglionic cells belong, not to the N. Vomeronasalis, which is evidently a specialised bundle of the olfactory nerve, but indeed to the N. Terminalis.

While JOHNSTON however was still of opinion that the peripheral termination of the N. Terminalis was limited, principally in any case, to the region of the N. Vomeronasalis, these investigators discovered that this ending is to be found in the foremost part of the nasal septum, reaching caudally to the rear border of the Organon Vomeronasale. It is only a small part of the peripheral branches that reaches this organ and the true olfactory mucous membrane, the region of the fila olfactoria, was free from branches of the N. Terminalis.

Through difference in tint the branches of the Terminalis could well be distinguished from those of the Trigeminal nerve (Nasociliary and Nasopalatine), which are also found in the mucous membrane of the nasal septum.

As will presently become clear, it is of importance in following the nerve to Amphioxus, that the N. Terminalis does not branch in the olfactory mucous membrane.

In 1912 and 1913 Mc. COTTER published his investigations on the N. Vomeronasalis and the N. Terminalis. By means of the dissecting microscope, thus as it were at magnifying glass magnification, he found the latter in the adult dog and cat, but not in the rat, the rabbit, the sheep, the guinea-pig or the oppossum. That he did not find it is not to be wondered at considering his method. His opinion that the N. Terminalis ends peripherally at or near the vomeronasal organ is also comprehensible because the bundles here are thicker, the fibres of the N. Terminalis being strengthened by those of the vomeronasal nerve.

This much as regards the *mammals*, which I have considered somewhat more extensively as most, and to my mind the most accurate, investigations have been done on them.

I can be brief about the birds, reptiles, and amphibians.

There does not seem to be much known about the N. Terminalis in the *birds*.

In the *frog* it was found in 1909 by C. Judson Herrick, who also described its central termination more especially; its peripheral branches could not be traced accurately. This was also the case in the *Urodela*, where the nerve was observed by Mc. Kibben (1914), who could not however find any ganglionic cells in it. Some time later Johnston succeeded in this. He says "In Amblystoma the nervus terminalis is ganglionated and supplies the vomeronasal organ, as in reptiles and mammals". Concerning the reptiles he says that the peripheral termination takes place "in the turtle to a medial diverticulum of the nasal sac, which presumably corresponds to the vomeronasal organ or a part of it".

We now come to the *fishes* wherein, setting aside an isolated observation by G. Fritsch about one of the Selachii, the nerve was first found by Pinkus in Protopterus. His preliminary communication appeared in 1894 in the "Anatomischer Anzeiger" and was followed in 1895 by his elaborate treatise "Die Hirnnerven des Protopterus annectens" in the "Morphologische Arbeiten". Pinkus found that his new nerve originates in the brain, places itself rostrally against the most mesial bundle of the olfactory nerve, takes its course over the nasal mucous membrane and is to be followed to the roof of the anterior nasal opening. The nerve consists of nonmedullated fibres and has in its course a cellular swelling, which is undoubtedly the Ganglion Terminale of later writers, although Pinkus could not convince himself of the ganglionic nature of the cells.

Sewertzoff (1902) found the nerve in embryos of Ceratodus. He mentions the fact, of importance for the homologisation, that the nerve does not branch in the olfactory mucous membrane and that it terminates in the skin at the external nasal opening. Soon (1904—1905) Bing and Burckhardt described the nerve in the adult Ceratodus also.

Concerning the *Selachii* the treatise of Locy, which appeared in the "Anatomischer Anzeiger" after several smaller publications, is well known. In this treatise, which is accompanied by a large number of handsome illustrations, he described the structure and development of the nerve in Acanthias as seen in series of sections, as well as its course as this is to be seen, by means of the dissecting microscope.

in 20 genera of sharks and rays. At first he held the nerve to be a part of the olfactory nerve, but later on he recognised its homology to the new nerve of PINKUS, and called it the N. Terminalis.

In the Selachii the distance between the nasal sac and the olfactory bulb is small, hence the olfactory nerve is short. Immediately on its appearance out of the nasal sac it is separated into a lateral and a mesial bundle by a small groove into which the distal termination of the N. Terminalis enters.

Scoliodon terrae novae alone has something peculiar. Here the two bundles are not only completely separated from each other, but the division also continues on to the bulb, and even to the distal (foremost) end of the tract, which usually is long in the Selachii. After the N. Terminalis of the Selachii has made its appearance out of the hemisphere, it takes its course along the mesial border of the tract, and when it has reached the bulb it forms a ganglion. In some species two ganglia were observed in the course of the nerve.

LOCY assures that the nerve in its distal ramifications is principally limited to the olfactory mucous membrane, but to my mind he has not proved this. His method was not sufficient to do this, and considering the results of other investigators in other classes of animals this assertion needs corroboration by preparations treated with silver compounds.

In the *Ganoids* the N. Terminalis was first found and clearly represented by PHELPS ALLIS (1897, fig. 64) in Amia calva. He could follow it caudally up to the fore-brain. In the larvae he also found its ganglion.

In 1910 BROOKOVER described its development in these fishes. His investigation contains many new finds and interesting communications, but his conclusion that the nerve is a branch of the olfactory nerve cannot in my opinion be correct. In his work in 1914 on the nerve in Lepidosteus he also came to this conclusion.

In the *Teleostei* SHELDON and BROOKOVER (1909) found the nerve in the carp and in Amiurus. According to them the roots of the ganglion enter the olfactory bulb to reach the hemisphere, contained in the tract. Here however the question arises whether they have not made a mistake analogous to that of DE VRIES in the embryos of man, as this is not the condition in the Dipnoi, in the Selachii, in the amphibians or in the mammals, nor either in man according to what BROOKOVER himself (1914) found in the last-named.

Concerning the lungfishes I can here demonstrate to you two fine models of the fore-end of the brains, with the nerves arising therefrom, of Ceratodus and Protopterus, both constructed by Dr. VAN DER

Horst in the Institute for Brain Research of Dr. Ariëns Kappers, who was so kind as to lend them for this evening. One sees the N. Terminalis arising out of the hemisphere, and running rostrally quite independent of the olfactory lobe, as is also the case in man according to Brookover (c.f. fig. 1).

Finally I come to *Amphioxus*, on whose cerebral nerves I published a communication in the meeting of the Royal Academy of October the 27th. 1894. As is known the trigeminal nerve of the craniata forms a complex of two dorsal segmental nerves, the components being the N. Ophthalmicus profundus (N. Nasociliaris) and the rest of the N. Trigeminus. I found both these components in the two nerves, of which the one appears before and the other behind the first well developed myotome (which has morphologically to be considered as the second). Before the homologue of the profound ophthalmicus, however, there is in Amphioxus still another nerve which supplies the utmost point of the snout. On account of this and because it arises from the morphological fore-end of the cerebral ventricle I called it the N. Apicis.

At first I thought that the N. Apicis would be aborted in the higher chordata, but shortly before the publication of my article the preliminary communication of Pinkus appeared (Anat. Anz. 1894), in which he reported the discovery of a new nerve in Protopterus, later named the N. Terminalis by Locy.

This had to be considered the homologue of the N. Apicis considering its course, ramification and origin, not from the infundibulum as I concluded out of the preliminary communication, but near the Lamina Terminalis as became clear when the more extensive treatise appeared the next year.

I must acknowledge that I have later on sometimes doubted whether this homologisation were correct, when I read the investigations of Locy in the Selachii, of Brookover and Sheldon in the Ganoids and Teleostei, and of Ernst de Vries and Döllken in the mammals, because all these writers assert that the peripheral termination of the N. Terminalis is wholly or principally limited to the olfactory mucous membrane (or in mammals to the vomeronasal organ, which is covered by a split-off part of the olfactory mucous membrane). In Amphioxus on the other hand the N. Apicis stands in no relation whatever to the covering of the olfactory groove.

After however reading the research of Huber and Guild (1913) this doubt was dispelled.

Their illustration (c. f. fig. 2) shows the N. Apicis of Amphioxus in the rabbit — I could almost say "in optima forma", even to the

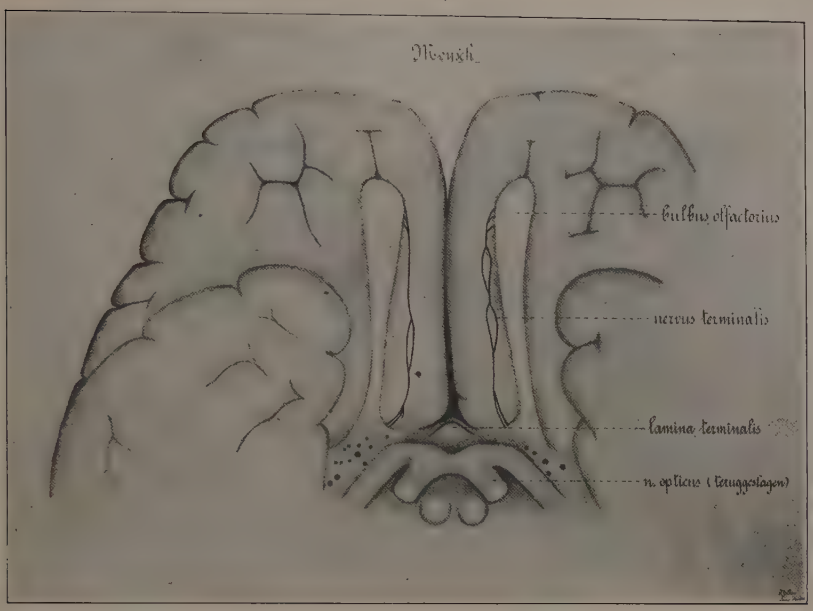

Fig. 1. Shows the lower surface of the foremost part of the brain of man and the intracranial part of the N. terminalis. (According to a figure of BROOKOVER, slightly modified).

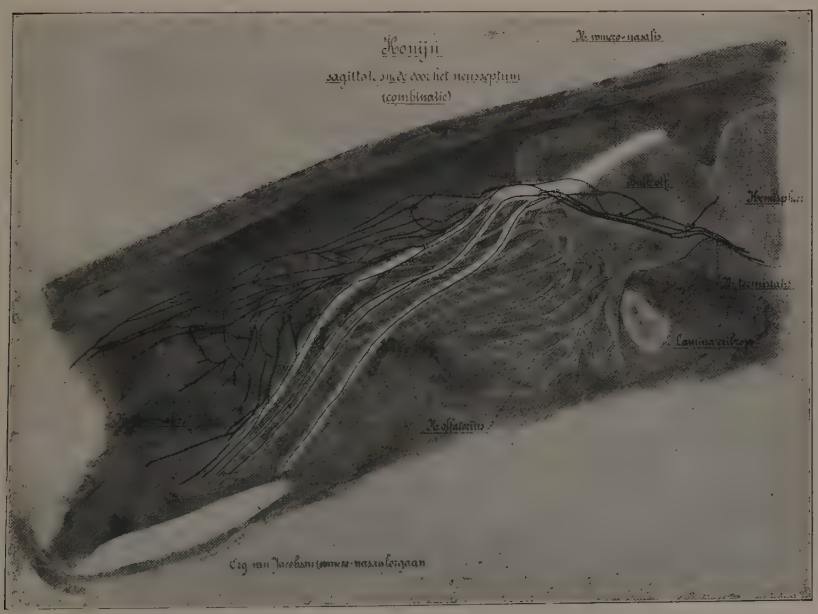

Fig. 2. Shows the mesial surface of the right olfactory lobe and of the contiguous part of the hemisphere with the nerves which radiate from this into the septum, after a combination of sagittal sections in the rabbit. (After a fig. of HUBER and GUILD, slightly modified).

disseminated ganglionic cells, which have already been long known in the N. Apicis.

As the N. Apicis is an ordinary cutaneous nerve [1]), the relation in which the N. Terminalis stands to the olfactory epithelium in some of the higher animals must be of a secondary nature. It is even possible that the terminal ramification of the nerve has become principally limited to the olfactory mucous membrane, as appears to be the case in many fishes.

Thus has the N. Terminalis completed its course through science in 20 years (1894—1914) beginning in the lung-fishes, I may as well add in Amphioxus, and ending in man. It can no longer be doubted that we have here to do with an independent cerebral nerve and not with a bundle of the olfactory nerve. In most or all of the craniata however branches of both nerves run close alongside of each other, and on account of this it is difficult to distinguish their peripheral distribution.

From Amphioxus to man the N. Terminalis is provided with disseminated ganglionic cells, which can partly be gathered together to one or more ganglia. On the other hand the olfactory nerve (including its specialised bundle, the N. Vomeronasalis of the Amniota) is distinguished by the complete absence of ganglionic cells.

At the end of this summary I want here to express my thanks to Dr. Ariëns Kappers, who was so kind as to send me for perusal a dozen treatises on the N. Terminalis, nearly all of American investigators, which have become the occasion of this address.

POST SCRIPTUM.

Early in March Dr. Kappers sent me for perusal a copy of a new work by Brookover, which he had received a few days earlier: "The Peripheral Distribution of the Nervus Terminalis in an Infant" (Journal of Comp. Neurology Vol. 28 N°. 2).

Brookover found the branching of the N. Terminalis in the nasal septum of the child analogous to that in the rabbit, according to Huber and Guild, only much more strongly developed. In it he could count about 1500 ganglionic cells, not considering the Ganglion

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[1]) It is a well known fact that ganglionic cells are found not only in the first but also in the second cutaneous nerve (N. Ophthalmicus prof.) of Amphioxus. De Quatrefages discovered them here in 1845 already, but held them for mucous cryptes, "cryptes mucipares". Incorrectly it is assumed that peripheral ganglionic cells are not present in the other nerves. I found multitudes of them in the nerves running under the atrial epithelium which covers the intestine and the liver.

Terminale. This ganglion was a compound of 6 to 8 ganglia, combined by a net of nervous fibres.

He mentions nothing about a N. Vomeronasalis, but found a stout nerve without ganglionic cells, which, with a branch of the N. Terminalis, passes through one of the hindmost openings of the Lamina Cribrosa to the nasal septum and anastomoses peripherally with the N. Nasopalatinus.

Brookover considers the above-named stout nerve as a sympathetic anastomosis between the Ganglion Sphenopalatinum and the Ganglion Terminale. To my mind this nerve is the N. Vomeronasalis, which has then not been aborted after birth, in man, as was hitherto the general opinion. In case this conjecture is correct, it must arise behind in the olfactory bulb and supply the vomeronasal organ.

This organ is generally present in the vertebrates higher than the fishes [1]), and seems to be a product of adaptation to terrestrial life. It first appears in the amphibians, and has been lost or is present only in the early stages of development in the higher forms which have secondarily become aquatic again (crocodiles, partly also the Chelonia, the Cetacea, and the Pinnipedia).

Flying also seems to be unfavourable for the development of the organ (birds and some — not all — of the bats).

The organ is usually named after Jacobson, who found it independently in a large number of mammals, and who also discovered the N. Vomeronasalis. His work became known through the report Cuvier made on it [2]).

After the considerable praise which Cuvier bestows on the work, for a part done in his laboratory, one would expect at the end of his report to the "Institut" the advice to have the treatise of Jacobson, "pensionnaire et chirurgien-major dans les armées de Roi de Danemark", printed. The end of the report, however, reads as follows: "Nous croyons que le Mémoire de M. Jacobson mérite l'approbation de la classe [de l'Institut] et que cet anatomiste doit être invité à continuer des recherches, qui ont déjà fourni un résultat aussi curieux".

This encouragement does not, however, seem to have had the desired result. At least it is not known that Jacobson has published his treatise, enlarged or not.

For the rest Cuvier makes a mistake in believing that nobody had observed the organ before Jacobson, and that it is not present

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[1]) C.f. R. Wiedersheim, Vergleichende Anatomie der Wirbeltiere, Jena, 1909.

[2]) G. Cuvier, Rapport fait à l'Institut, sur un Mémoire de M. Jacobson intitulé: Description anatomique d'un Organe observé dans les Mammifères. Annales du Muséum d'Histoire naturelle, Tome 18, 1811.

in man. It has escaped his attention that RUYSCH, who is cited by him à propos of the Meatus Nasopalatinus, (l.c. p. 414. He writes: RUISCH) is the discoverer of the organ, and just in man in whom it is normally present as was corroborated later on.

KÖLLIKER[1]) and HERZFELD[2]) found it regularly in children while it is seldom wanting in adults. When this was the case it had probably to be ascribed to former diseases of the nasal septum.

The description of RUYSCH[3]), who also gives a clear representation of the orifice of the organ, with a sound brought into it, on the nasal septum of a child, reads as follows: "In anteriore et inferiore parte septi juxta palatum in utroque latere foramen apparet, seu osculum cujusdam ductus de cujus usu et existentia nil apud authores legi; inservire muco excernendo existimo".

JACOBSON also, not knowing RUYSCH's work, is inclined to consider the organ as being secretory, although the powerful innervation pleads for a sensory function, but (l.c. p. 422): "quel agent extérieur pourroit aller se faire percevoir dans un réceptacle si caché, si profond, si peu accessible?"

CUVIER himself still thinks — under reserve — he has to accept a kind of olfactory perception and the later writers do this too. It is usually assumed that the organ serves to smell the food which has already been taken into the mouth; in mammals the odour would then rise up through the Meatus Nasopalatinus. This can however not be the case in the horse or the donkey (nor in the camel or giraffe), because here the Meatus is no longer opened to the buccal cavity, while their Organon Vomeronasale cannot be held to be rudimentary as is the case in man.

The secretory function is evident on account of the numerous glands (KÖLLIKER, l. c. p. 11) which fill the organ with mucus, which streams out through ciliary motion, but the difficulties against accepting

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1) A. KÖLLIKER, Ueber die Jacobsonschen Organe des Menschen. Reprinted from the Festschrift für RINECKER, Leipzig 1877.

2) P. HERZFELD, Ueber das Jacobsonsche Organ des Menschen und der Säugethiere, Zoologische Jahrbücher, Abth. für Anat. und Ontogenie der Thiere Bd. 3, 1889.

HERZFELD gives a summary of the mammals in which the organ had been found by him and others up to 1889, also in connection with the meatus nasopalatinus. He might have added that JACOBSON had also already observed it in the marsupials (kangaroo). Later on it was also found in the Monotremata and Edentata.

3) F. RUYSCH, Thesaurus anatomicus III, Amstelodami, 1724, p. 26, N°. LXI, 5. Illustration: Tab. IV, fig. 5.

KÖLLIKER (1877) cited the description, mentioned above, from an edition of 1703 p. 49; hence more than 100 years before CUVIER's report.

an olfactory function, already hinted at by JACOBSON, and which KÖLLIKER tries to evade in a peculiar manner, are not to be got out of the way.

In this regard an observation of HERZFELD in connection with the venous sinus, with a strong circular layer of nonstriated muscular fibres, which is found in the wall of the organ of the rat on the inner side of the bony capsule, — cartilaginous in the majority of the mammals — seems to me worthy of attention. He assumes that the air will be sucked into the organ through contraction of the sinus and the lessening of the volume of the wall, inside the rigid capsule, caused by this.

If this appears to be the case in other animals also — the opportunity for research will probably present itself in a veterinary college — then a sort of olfactory function would become comprehensible. It would then also become clearer why the Cetacea and Pinnipedia are nearly the only [1]) mammals in which the search for the organ [2]) of RUYSCH has been in vain.

It is comprehensible that the Cetacea and Pinnipedia have lost the true olfactory organ, adapted to aquatic life in earlier fishlike ancestors, it became adapted to smelling in the air in later ancestors, which lived on land as mammals, When these, in a still later period, again went back to aquatic life, as Protocetacea and Protopinnipedia, the true olfactory organ could not undergo this change and became rudimentary or disappeared altogether. If the organ of RUYSCH in terrestrial mammals is always filled with liquid (mucus), and does not need to adapt itself to smelling in the air, then there is not the same reason for its disappearance in the Cetacea and Pinnipedia as there is for the degeneration of the true olfactory organ of the Cetacea.

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[1]) One would expect the Sirenia here also. It is remarkable however that Manatus, according to STANNIUS (Lehrbuch 1846, p. 399) possesses an exceptionally well developed Organon Vomeronasale. In some bats and catarrhine apes the organ has disappeared through some cause or other, as in the Cetacea and Pinnipedia.

[2]) The numerous morphological investigations on this organ have taught us very little about its function. On histological grounds a sort of olfactory function is not to be doubted, (c.f. amongst others M. VON LENHOSSEK, Die Nervenursprünge und Endigungen in Jacobsonschen Organ des Kaninchens. Anat. Anzeiger. 1892). This is about the only result, concerning the function which we can, after about 200 years, add to the words of the discoverer: "Inservire muco excernendo existimo."

Microbiology. — *"The significance of the tubercle bacteria of the Papilionaceae for the host plant"*. By Prof. BEIJERINCK.

(Communicated in the meeting of April 26, 1918).

As there is no reason to doubt of the accuracy of HELLRIEGEL's [1]) experiments, it appears certain that the bacteria of the nodules on the roots of the Leguminosae are indispensable for the fixation of atmospheric nitrogen by these plants. [2]) But I shall prove that the theory, at present generally adopted, according to which this process takes place only within the tubercles, cannot be correct. But previously some remarks on the occurrence of the tubercles and the cultivation of bacteria from them.

For some plant species such as serradella (*Ornithopus sativus*) and the yellow lupine (*Lupinus luteus*), it cannot be doubted that only the tubercle-bearing specimens grow vigorously in nitrogen-poor soils and consequently, after the theory, fix the atmospheric nitrogen. It is therefore easy on poor heath fields to find languishing, stunted lupine plants, always devoid of nodules, amid the luxuriantly growing tubercle-bearing ones. Never did I find there well-developed lupine or serradella plants quite without them. But the number of tubercles is of no consequence, it evidently suffices if only few come to development.

In garden experiments on open sandbeds, without supply of nitrogen, but where inevitably more nitrogen compounds occur than in heath soils, also in peas and beans (*Vicia faba*), plants with nodules grow better than those devoid of them.

In fertile garden soil such as in the laboratory garden at Delft, yellow lupine and serradella do not fully develop, and especially their roots make the impression of sickliness; tubercles do not grow on them, not even when the soil has been abundantly provided

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[1]) H. HELLRIEGEL und H. WILFARTH, Untersuchungen über die Stickstoffnahrung der Gramineën und Leguminosen, Zeitschrift für Rübenzuckerindustrie, Beilageheft November 1888. See further the excellent treatise of HILTNER, Bindung von freiem Stickstoff in höheren Pflanzen, in Handbuch der technischen Mykologie, Bd. 3, 1903—1905.

[2]) For the objective proof that here free atmospheric nitrogen is fixed see, besides HELLRIEGEL (l. c. p. 191), SCHLÖSING et LAURENT, Fixation de l'azote libre par les plantes, Ann. de l'Institut Pasteur, Tome 6, pag. 65, 1892.

with the concerned bacteria. Whether the latter die in the soil or are not attracted by the roots of the plant is not yet clear. Most other leguminous plants, such as clover, *Vicia*, peas and *Vicia faba*, bear also in fertile soil many nodules, and it is not easy to find specimens wholly devoid of them, unless the soil has been previously sterilised.

On the roots of *Genista anglica* and *Genista pilosa*, growing on poor heath fields, I found after long seeking only very few tubercles, although they and in particular the former, bore many pods with good seeds; the tubercles are, however, never quite absent. When sown in my garden at Delft or brought there as plants, they die after some few years. On the other hand, *Genista tinctoria* thrives as well at Delft as along the highway of Zutphen to Vorden and at both places bears a small number of nodules.

For *Robinia pseudo-acacia* the favourable influence of *B. radicicola* only on the young plant, has been stated by Nobbe. [1]) As to full-grown specimens on poor heath soil at Gorssel I could after long digging find but few tubercles, while at a small distance, but on somewhat better soil more tubercles occurred, but still so little numerous, that nobody would attribute to them any direct significance for such a large tree, had not the fixation of nitrogen in the tubercles become an inveterate belief. *Sarothamnus vulgaris* and *Ulex europaeus* behave in the same way as *Robinia*. On *Phaseolus vulgaris* on sandy soils I found but few nodules, and then only on thin rootlets and nearly always enclosed by plant remains; in the pure sand the nodules are very rare. In garden soil at Delft *Phaseolus* produces no nodules, but it does in a there arranged sandbed; *Lupinus luteus* and *Serradella* behave likewise.

When comparing the various mentioned plants, all noted in agriculture for their power of ameliorating the soil, as they contain in their dry substance nearly double the quantity of nitrogen found in other plants, for example the grasses, we come to the conclusion that only for lupine and serradella the number and weight of the tubercles is of some significance in regard to the whole weight of the plant. For other species they are of so little volume that even if within them free nitrogen were fixed with great intensity, only an extremely little quantity of fixed nitrogen could be expected, whilst in reality this amount is very considerable. Hence the theory, at present generally accepted, after which the fixation takes place in the

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[1]) Hiltner l.c. Also Büsgen, Bau und Leben unserer Waldbäume, 2te Aufl., Pag 246, 1917.

nodules only, requires reconsideration. Also other experiences make this reconsideration necessary. But previously a few remarks on the isolation of the bacteria from the nodules and from other materials, and on the question of their specificity.

A very convenient medium for isolation was already described in 1888, [1]) namely pea leaves- or clover-extract-gelatin with 2 % cane sugar. *B. radicicola* grows thereon in soft, white, non-liquefying colonies, while *B. ornithopodis* from *Ornithopus perpusillus*, *O. sativus* or *Lupinus luteus*, when isolated in the autumn or in March, liquefy somewhat, as does *B. herbicola*. [2])

As a solid medium, poor in nitrogen compounds, I recommend a plate of: Tapwater 100, agar 2, cane sugar 1, starch 1, bipotassiumphosphate 0,05, in which, because of the albuminous matter of the agar, enough fixed nitrogen is present to cause a distinct growth of *B. radicicola*, but the colonies remain small. Later a little saltpetre or ammoniumsulphate may be added locally, which makes the tubercle bacteria like the other saprophytes thrive well, showing that they do not assimilate the free atmospheric nitrogen. If on such a plate eventually germs of *Azotobacter*, which is able to assimilate free atmospheric nitrogen, are present, these will grow quite well if no nitrogen compounds are added. Such nitrogen-poor plates are also useful to recognise the spore-bearing soil bacteria, which almost constantly appear at the isolation of *B. radicicola*.

I only call tubercle bacteria those species which develop mutually identic colonies by thousands or hundreds of thousands from the externally well-sterilised and cautiously crushed nodules. These bacteria derive for the greater part from within the cells. I consider the deviating and less numerous colonies obtained at the culture experiments as the product of germs accidentally present in the intercellular cavities of the rind of the nodules. [3]) That the full-grown bacteroïds cannot develop on the plates is well-known; hence bacteria may be expected from the tubercles only in the beginning of their development.

It is an important and until now not yet sufficiently investigated circumstance that from the tubercles of the same plant not always the same bacteria are obtained. So I found for *Ornithopus perpusillus*

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[1]) Botan. Zeitung. 1888 Pag. 764.

[2]) Occasionally a great number of colonies of *B. herbicola* are obtained from the tubercles; whoever is unacquainted with this species may make misfakes in the isolation of *B. radicicola*. But even with this knowledge the isolation of serradella- and lupine-bacteria is difficult. Good descriptions of these forms do not exist.

[3]) Besides *B. radicicola* *B. herbicola* can also occur *within* the living cells.

the bacteria I had isolated in March different from those grown in October, whilst the tubercles came from plants growing side by side and being in the same state of development. With the yellow lupine and serradella I had similar results. In most other cases, however, for example with *Pisum*, *Lathyrus*, *Vicia*, and *Trifolium*, the similarity of the various mutually independently isolated stocks is so complete and the image of *B. radicicola* can so distinctly be recognised, that the above observation requires nearer confirmation. But we cannot now enter upon this point.

When trying to isolate *B. radicicola* from materials other than the nodules, for example from the soil and from the dying surface cell-layers of the root, it proves very difficult to recognise this species amid the numerous other saprophytes, especially when the number of the germs of the different species is to be determined quantitatively. *B. fluorescens liquefaciens* causes much trouble by the liquefying of the gelatin plates, and yet it is necessary to use these plates as on them the colonies of all the species lie free from one another, while on agar they are overgrown and rendered unrecognisable by *B. fluorescens*, which extends strongly sideways.

Concerning the question if only one or more species of tubercle bacteria exist the following.

Already in 1892 experiments thereabout were made by the late HELLRIEGEL [1]) in the experimental station at Bernburg with pure cultures of the bacteria made by myself at Delft. Of his results HELLRIEGEL sent me two reports. In the first, dated 24 July 1892, he gives as "Augenblickliches Hauptresultat: "Es gelingt mit den Reinkulturen von *B. radicicola* var. *Pisi* oder von *Vicia faba*, die Erbsen und Bohnen, und mit denen des *Bac. radic.* var. *Lupin.* oder *Ornithopodis* Lupinen und Serradella erfolgreich zu infiziren und zum Wachstum resp. der Assimilation des freien Stickstoffs zu bringen, und das ist was unsere anfängliche Behauptung bestätigt". Already earlier HELLRIEGEL had arrived at the conclusion that the bacteria of *Lupinus* and *Ornithopus* belong to a species different from that of *Pisum* and *Vicia*, which was also my own opinion.

In later years many interesting experiments were made in this direction, especially by HILTNER. Yet the evidence is unsatisfactory as it proved hitherto impossible in the sand cultures [2]) to bring Leguminosae to complete development by infection with

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[1]) He died 24 September 1895 of a stomach disease and was already suffering when I visited him at Bernburg in 1892.

[2]) It is a well-known fact that the Papilionaceae, when cultivated in liquids, do not fix the atmospheric nitrogen indifferently whether they produce tubercles or not.

B. radicicola only and with exclusion of all other microbes. Such cultures are always at the end of the vegetation period rich in various other species, in particular in *B. fluorescens liquefaciens* and the nitrogen-fixing spore-forming *Granulobacter* (*Clostridium*) *pasteurianem* and *Helobacter cellulosae*. This observation holds good as well for the first experiments made by myself as for those of others, and this should never be lost sight of when reading the descriptions of the infection experiments with the so-called "pure cultures". It had not escaped HELLRIEGEL's attention, and we see it in all the photographs of his above mentioned treatise at the film of the glass vessels, wherein he cultivated his plants (in bright daylight), which film consisted of Chlorophyceae and various other species of microbes, but he thought it of no consequence (l. c. p. 169). For myself I have observed in nitrogen-free sand, besides the mentioned species, *Chlorella* and *Cystococcus* and sometimes also *Palmella cruenta* and many Cyanophyceae. Many of my later efforts to bring clover plants to complete growth on agar with nutrient salts and *B. radicicola* in large cotton-plugged ERLENMEYER-flasks, failed as the plants ceased to grow before they blossomed, although the nodules developed very well.

The tubercle bacteria do not fix the atmospheric nitrogen when cultivated in nutrient media.

I will now call attention to my chief subject namely the want of power of the tubercle bacteria to fix the free atmospheric nitrogen. They do this neither when cultivated out of the plant nor within the nodules.

Regarding the first point the experiment is very simple. We have but to crush the nodules and bring the thus obtained material into culture soils used for the ordinary experiments to fix free nitrogen and then cultivate at 20° to 30° C.; or we use the pure cultures for infection of the same media. A convenient medium is: Tapwater 100, Glucose 2, Dikaliumphosphate 0,05, lime 2, fresh garden soil 2. This liquid, to which the garden soil is added as a catalyst, must previously be sterilised to kill the germs of *Azotobacter*, *Granulobacter* and *Helobacter*; notwithstanding the sterilisation, the soil preserves its catalytic power very little impaired. The spores of the nitrogen-fixing *Helobacter* and *Granulobacter* often adhere to the nodules and, when present, fermentation phenomena show that the experiments cannot be relied upon, *B. radicicola* not causing fermentation. Commonly, however, these fermenting and nitrogen-

fixing microbes can be removed by thoroughly washing of the nodules with alcohol and water. In the course of many years I have experimented in this way with numerous species of tubercle bacteria, and with many modifications in the nutrient media as well in the temperature as in the source of carbon. Moreover I have, as said, tried to grow pure cultures of the bacteria themselves in the liquid culture medium as also on solid culture soils of various compositions, and at first I thought I had observed a rather considerable increase of these organisms. This increase, however, proved to be really very slight, so slight that gain of atmospheric nitrogen is not proved, whilst the obvious augmentation of dry weight of the sown bacteria derives from the formation of thick slime walls, that is of nitrogen-free, cellulose-like substances around the hardly augmented original protoplasmic material. [1])

Only when cultivating the microbes in plant extracts with cane sugar, wherein nitrogen compounds are evidently present, I could observe a very slight and by no means convincing increase of the total nitrogen rate of the liquid in consequence of the growth of *B. radicicola*. But when performing these experiments I was not yet acquainted with the circumstance that laboratory air contains sufficient carbon and nitrogen compounds to be made perceptible by the growth of microbes which can feed on them. This was afterwards demonstrated by Ir. A. VAN DELDEN and myself in our investigation on *Bacillus* (*Actinobacillus*) *oligocarbophilus*. [2])

There exists moreover an aërobic spore-producing bacterium [3]), hard to kill by sterilisation of the nutrient liquids, which fixes free nitrogen ; at that time it was still quite unknown to me and even now it is very imperfectly understood. It may have been present at my experiments likewise as at those of other investigators who think they have observed fixation of free nitrogen out of the plant in the pure cultures of *B. radicicola*.

With sufficient precautions the results of such experiments are however always the same: The bacteria of the nodules do in no way fix the free atmospheric nitrogen. When the experiments are performed, not with

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[1]) The slime formation is of importance for the explanation of the "slime threads" (erroneously called "infection threads") within the nodules. See "Die Natur der Fäden der Papilionaceënknöllchen." Centralbl. für Bakteriologie. Bd. 15, pag. 928, 1894.

[2]) Ueber eine farblose Bakterie deren Kohlenstoffnahrung aus der atmosferischen Luft herrührt. Centralbl. f. Bakteriologie 2te Abt. Bd. 10, pag. 33, 1903.

[3]) *Bacillus danicus*, T. WESTERMANN and F. LÖHNIS, Centralbl. f. Bakteriologie. 2te Abt. Bd. 22, pag. 250, 1909).

nutrient liquids, but with a solid medium, the results are quite the same: fixation of nitrogen does not take place then either. Stress must be laid on the latter fact as it seems impossible to fix free nitrogen by the Papilionaceae when cultivated in liquid media even under the best circumstances and whether tubercles are produced or not. So it seems probable that for this process a direct contact with the air is necessary, which cannot be realised in the liquid culture media, but very well in solid ones.

Further it must be observed that the plate cultures of some of the nodule organisms,[1]) for example the forms from *Pisum*, *Vicia*, and *Trifolium*, on glucose-agar-potassiumphosphate plates, in absence of purposely added nitrogen compounds, at superficial view make the impression of being quite able to develop, but here too, it is only the formation of much wall substance, as already described above, and not of nitrogen-rich protoplasm, which explains the voluminosity of the colonies.[2]) With other slime-producing bacteria, as *B. radiobacter* and *Aerobacter viscosum*, of which it is quite certain that they cannot live on the atmospheric nitrogen, extensive colonies may likewise be grown on the said nitrogen-poor medium with fit carbon food. By a better nitrogen nutrition such colonies may even be greatly reduced in volume, the wall substance then serving as food under a strong increase of the bacterial protoplasm, which gives rise to very interesting experiments. It is only when being acquainted with these facts by personal observation that we can understand how in the literature so many statements can occur on the nitrogen fixation by the nodule bacteria, which does not take place.

Within the nodules the atmospheric nitrogen is neither fixed.

The preceding gives rise to the question, whether the protoplasm of the host plant might be the catalyst that enables the invading bacteria, in their bacteroidal state, to fix the free nitrogen. However improbable this hypothesis may appear, being in contradiction with the laws of heredity, still it deserves attention because the rate of

[1]) The wonderful "experiments" of Mazé (Annales de l'Institut Pasteur T. 11, pag. 44, 1897, T. 12, pag. 1 and pag, 128, 1898), who asserts that on broth gelatin plates at the same time ammoniumcarbonate is produced and fixation of free nitrogen by *B. radicicola* takes place, need not be considered, although they are taken up uncritisised in the handbooks of Plantphysiology.

[2]) Likewise for the ordinary saprophytic bacteria the want of nitrogen compounds varies very much: the large-celled *Bacillus megatherium* requires very little, the small celled *Bacterium fluorescens* very much.

albuminous matter in the nodules is so very high. I myself found about 4 % nitrogen, which is about 25 % albumen in the dry matter of pease-nodules. Others found 5 to 6 % nitrogen. It is noteworthy that the bacterial colonies on agar plates, grown out of the plant, contain but 1 to 2 % nitrogen of the dry weight, which consists for the greater part of carbohydrates. So it is certain that the bacterial body is very much modified by its entrance into the plant cell as well morphologically as physiologically. Therefore it was tried gazometrically to state nitrogen absorption in the tubercles. If the hypothesis is founded it must be possible, with a great quantity of tubercles in a closed space and under favourable physiological conditions, easily to observe that absorption. For the number of tubercles, for example of the woody papilionaceae, being as said very small, while yet these plants are noted in agriculture for their considerable nitrogen-fixing power, the action of the tubercles must necessarily be very intense.

To test the hypothesis we acted as follows. [1]) First small, later larger quantities of lupine and serradella tubercles were placed in wide glass tubes which could readily be connected with the gas burettes, then put in thermostats at about 25° C. The tubercles respiring vigorously we had to keep account with a rapid assimilation and supply of the oxygen. Further it was only necessary to determine the quantity of nitrogen still present after deduction of the carbonic acid and the oxygen. The only difficulty we met with was that the nodules, which by their abundant content of albuminous matter are an excellent food for bacteria, when they touch each other and get moist, easily give rise to fermentations in particular by *Bacterium aërogenes*. Hereby hydrogen and much carbonic acid are produced, so that it is then necessary also to determine the hydrogen. But this fermentation may be prevented by introducing the material very loosely into the burette, so that there are but few points of contact between the nodules, and the air can freely pass between. Under such conditions there is no danger that free nitrogen will be formed; this only occurring through the action of the denitrifying bacteria on nitrates, which substance is in the nodules completely absent.

Of the tubercles of yellow lupine we used in our experiments quantities of 100 grs., 500 grs., and later even of 1 kil. In some

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[1]) In some of these experiments I was assisted by Ir. D. C. J. Minkman, formerly assistant to the Laboratory for Microbiology of the Technical High School at Delft.

experiments we had the root tubercles cut off, in others the roots with the tubercles were left united with large pieces of the stem, so that eventually formed nitrogen compounds might be able to flow into the stem. All our estimations, however, showed that not in a single case the slightest fixation of nitrogen by the tubercles was observable. As at first we doubted of the accuracy of our results obtained with relatively little material, we afterwards used the just mentioned larger quantities, but this did not make any difference either. Besides the two said species we still examined several times 10 to 20 grs. of the nodules of *Vicia faba*, and once about 15 grs. nodules of *Robinia pseudo-acacia*, but other results were not obtained.

As our researches did not last longer than 12 to 20 days it might be objected that we have not sufficiently imitated the conditions of the plants in the field. Further, that in these experiments the growth of the tubercles, together with that of the whole plant, was excluded. Although these objections have not been refuted in the preceding, it is still highly improbable that nitrogen fixation would be associated with the growth of the tubercles and not with the augmentation of the bacteria out of the plant. Principal, however, is the fact that if within the nodules nitrogen fixation were to take place, which might have escaped our attention, the concerned quantity must certainly be extremely small. When we now consider how difficult it is to collect a few grams of tubercles for example of *Robinia*, it is clear that if this material is to be of any significance for such a great tree, its nitrogen-fixing power must be enormous. The experiments, however, show that the tubercles are wholly inactive or nearly so, hence there can be no question of attaching to them any importance concerning the nitrogen nutrition, whilst yet nitrogen fixation by this tree is as certain as for lupine and serradella and even on a much larger scale. So the nitrogen nutrition of the Papilionaceae can only be indirectly connected with the bacteria of the nodules. In my opinion this relation can only exist in the herbaceous species and in the germ plants of the shrubs and trees of that plant order, but in full-grown specimens of the woody species such as *Robinia pseudo-acacia* the presence or the absence of the nodules is wholly indifferent. Likewise on the roots of shrubs, such as *Sarothamnus vulgaris*, *Spartium scoparium*, *Genista anglica*, and *Genista pilosa* in full-grown condition, the number of tubercles is so small, their volume so insignificant to that of the whole plant, that even if they were able to assimilate some free nitrogen their slight activity could not possibly explain the rich nitrogen store of the whole plant.

Hence, the at present generally accepted explanation of the peculiar

behaviour of the Papilionaceae cannot be correct. New researches, especially with *Phaseolus*, are desirable.

From the preceding follows:

For various Papilionaceae, excelling by their abundance of nitrogen compounds, even when cultivated in media without such compounds, the number and volume of the tubercles is so small, that if only within them the fixation of free nitrogen should take place, the intensity of the process in these tubercles must necessarily be very great. We have not, however, succeeded gazometrically in observing the process in the tubercles at all.

Neither do the tubercle bacteria fix the atmospheric nitrogen when cultivated out of the plant in nutrient liquids or in plate cultures, nor enclosed in solid media.

The contradictory statements in the hand books of Plantphysiology are erroneous.

Physics. — *"On the rotational oscillations of a cylinder in an infinite incompressible liquid"*. By D. COSTER. (Communicated by Prof. J. P. KUENEN).

(Communicated in the meeting of May 25, 1918).

The method to be followed in the discussion of the problem will be in the main the same as that used by Prof. VERSCHAFFELT in the analogous case of the sphere[1]). We consider the rotational swings about its axis of an infinitely long cylinder which executes a forced vibration. Our object will be to ascertain the motion in the liquid which will establish itself after an infinite time (in practice after a relatively short time[2])) in order to compute the frictional moment of forces exerted on the cylinder by the liquid. For the sake of simplicity the calculations will be referred to a height of 1 cm.

The motion of the cylinder may be represented by $\alpha = a \cos pt$ where α is the angle of rotation. An obvious assumption to be made is that the liquid will be set in motion in coaxial cylindrical shells each of which will execute its oscillations as a whole. On this assumption it is not difficult to establish the differential equation for the motion of the liquid.

Let ϱ be the density of the liquid.

μ the viscosity of the liquid.

ω the angular velocity of a cylindrical shell.

r the radius of the shell.

The frictional force per unit surface of one of the shells will then be $F = r\mu \frac{\partial \omega}{\partial r}$ and the frictional couple on a cylindrical surface of radius r : $2\pi r^3 \mu \frac{\partial \omega}{\partial r}$.

Taking a shell of thickness dr its equation of motion will be

$$2\pi r^3 \, dr \, \varrho \frac{\partial \omega}{dt} = \frac{\partial}{\partial r} \left\{ 2\pi r^3 \mu \frac{\partial \omega}{\partial r} \right\} dr,$$

which reduces to

$$\frac{\varrho}{\mu} \frac{\partial \omega}{\partial t} = \frac{\partial^2 \omega}{\partial r^2} + \frac{3}{r} \frac{\partial \omega}{\partial r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

[1]) Comp. Proceedings 18 p. 840. Sept. 1915. Comm. Leiden 148*b*.

[2]) Comp. Comm. 148*b*. pag. 22 footnote.

It is important to note that equation (1) may also be deduced from the general equation of hydrodynamics without its being necessary to neglect the second power of the velocities, as is the case in many problems of that kind. For an infinitely long time of vibration i. e. for uniform rotation (1) simplifies to

$$0 = \frac{d^2\omega}{dr^2} + \frac{3}{r}\frac{d\omega}{dr} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The solution of (2) is $\omega = \frac{c_1}{r_2} + c_2$, c_1 and c_2 being integration-constants. If the solid cylinder (radius R) rotates with uniform speed Ω in an infinite liquid, the result will be $\omega = \frac{R^2\Omega}{r^2}$, giving for the frictional couple as is well known the expression

$$-4\pi\mu R^2\Omega. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2')$$

In order to arrive at a possible solution of (1) we have to make our assumption regarding the motion of the liquid a little more definite by assuming that the angular displacement of each shell is represented by

$$\alpha_r = f(r)\ cos\ (pt - \varphi(r)). \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

We may also consider (3) as the real part of the complex function ue^{ipt}, where u is a function of r the module of which gives the amplitude of the oscillation and the argument the phase-shift $q(r)$. Remembering that $\omega = \frac{\partial\alpha}{\partial t}$ equation (1) may be reduced to

$$\frac{d^2u}{dr^2} + \frac{3}{r}\frac{du}{dr} - \frac{i\varrho\, pu}{\mu} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Equation (4) is closely related to the differential equation of the cylindrical functions. Indeed by the substitution $y = zv$ BESSEL's equation of the 1st order $\frac{d^2y}{dz^2} + \frac{1}{z}\frac{dy}{dz} + \left(1 - \frac{1}{z^2}\right)y = 0$, changes to

$$\frac{d^2v}{dz^2} + \frac{3}{z}\frac{dv}{dz} + v = 0.$$

It follows that the general solution of equation (4) is

$$u = \frac{1}{r}\{A\,J_1(cr) + B\,N_1(cr)\}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $c = \sqrt{\frac{-i\varrho p}{\mu}}$, A and B being complex integration-constants.

J_1 is the cylindrical function of the 1st kind and 1st order, N_1 that of the 2nd kind and 1st order [1]).

As regards c an agreement must be come to. We shall choose the root with the negative imaginary part i.e. $c = ke^{-\frac{i\pi}{4}}$, where $k = |c| = \left|\sqrt{\frac{\varrho p}{\mu}}\right|$.

As a first boundary-condition we have $\underset{r=\infty}{Lim}\, r a_r = 0$ [2]). As this relation must hold for all values of t, it follows that $\underset{r=\infty}{lim}\, ru = 0$.

The cylindrical functions with complex argument all become infinite at infinity with the exception of the so-called functions of the 3rd kind or HANKEL's functions $H_p^{(1)}$ and $H_p^{(2)}$. Of these $H_p^{(1)}$ disappears at infinity in the positive imaginary half-plane and on the contrary becomes infinite in the negative half, whereas the opposite is true for $H_p^{(2)}$. By our choice of c in the negative imaginary half we are led to the function $H_1^{(2)}$. For the integration-constants in equation (5) this gives the relation $B = -iA$ [3]), so that (5) becomes

$$u = \frac{A}{r} H_1^{(2)}(cr) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

For the determination of A we have to use the 2nd boundary-condition $a_R = a \cos pt$, R being the radius of the cylinder. We therefore assume that there is no slipping along the wall.

Hence $A = \frac{aR}{H_1^{(2)}(cR)}$,

so that

$$a_r = \mathrm{R} \frac{aR}{H_1^{(2)}(cR)} \frac{H_1^{(2)}(cr)}{r} e^{ipt} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The symbol R is intended to indicate, that the real part has to be taken of the function which stands after it.

If we had chosen for c the root with the positive imaginary part, we should have had to utilize the function $H_1^{(1)}$. It is quite easy to verify that this would not have made any essential change in the solution (7).

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1) Comp. JAHNKE u. EMDE. Funktionentafeln pp. 90 and 93.
NIELSEN. Cylinderfunktionen. Instead of N NIELSEN uses the symbol Y.

2) Prof. VERSCHAFFELT puts $\underset{r=\infty}{Lim}\, \alpha_r = 0$, which in my opinion is not quite correct, as the *linear* velocity has to disappear at an infinite distance. Comm. 148*b* p. 22.

3) Between J, N, and H a linear relation holds. Comp. J. u E. p. 95.

For large values of x (real, positive) $H_1^{(2)}(x\sqrt{-i})$ approaches asymptotically to

$$-\frac{e^{-\frac{x}{\sqrt{2}}}}{\sqrt{\tfrac{1}{2}\pi x}}e^{-i\left(\frac{x}{\sqrt{2}}-\frac{\pi}{8}\right)};$$

therefore for $(k\ R)$ sufficiently large:

$$\alpha_r \approx -\frac{aR}{|H_1^{(2)}(cR)|}\frac{e^{-\frac{kr}{\sqrt{2}}}}{\sqrt{\tfrac{1}{2}\pi k}\, r^{1\frac{1}{2}}}\cos\left(pt-\frac{kx}{\sqrt{2}}+\frac{\pi}{8}-\varphi\right) \quad . \quad (8)$$

where $\varphi =$ argument $H_1^{(2)}(c\ R)$.

From (8) it appears that damped waves are propagated from the cylinder to infinity, the velocity of propagation being

$$v=\frac{p}{k/\sqrt{2}}=\frac{p\sqrt{2}}{k}=\sqrt{\frac{2p\mu}{\varrho}}$$

and the wave-length

$$\lambda = vT=\frac{2\pi v}{p}=\frac{2\pi\sqrt{2}}{k}=2\pi\sqrt{\frac{2\mu}{\varrho p}}. \quad . \quad . \quad . \quad . \quad (8')$$

The frictional moment on the wall of the vibrating cylinder is $2\pi\mu R^3\left[\frac{\partial\omega}{\partial r}\right]_R$ where $\omega=\frac{\partial\alpha}{\partial t}$. First we determine $\left[\frac{\partial\alpha r}{\partial r}\right]_R$ from (7)

$$\left[\frac{\partial\alpha_r}{\partial r}\right]_R = \mathrm{R}\left[-\frac{a}{R}e^{ipt}+ac\frac{H_1^{(2)'}(cR)}{H_1^{(2)}(cR)}e^{ipt}\right] \quad . \quad . \quad . \quad . \quad (9)$$

For the reduction of the 2nd part on the right hand side of (9) we make use of the well-known recursion-formula of the cylindrical functions:

$$\frac{dH_1^{(2)}(z)}{dz}=H_0^{(2)}z-\frac{1}{z}H_1^{(2)}(z)$$

By its application (9) obtains the form

$$\left[\frac{\partial\alpha_r}{\partial r}\right]_R = \mathrm{R}\left[-\frac{2a}{R}e^{ipt}+ac\frac{H_0^{(2)}(cR)}{H_1^{(2)}(cR)}e^{ipt}\right]. \quad . \quad . \quad . \quad (10)$$

giving for the frictional couple

$$K=2\pi\mu R^3\left[\frac{\partial\omega}{\partial r}\right]_R=-4\pi\mu R^3\omega+\mathrm{R}\frac{d}{dt}\left[2\pi\mu R^3 ac\frac{H_0^{(2)}(cR)}{H_1^{(2)}(cR)}e^{ipt}\right] \quad (11)$$

For an infinite time of swing, i. e. $p=0$, but with a rotational velocity differing from 0, $|c|=\sqrt{\frac{\varrho p}{\mu}}$ becomes 0. In that case the

second term on the right of (11) disappears on two grounds: (1) because $c = o$ (2) $\underset{cR=0}{Lim} \frac{H_0^{(2)}(cR)}{H_1^{(2)}(cR)} = 0$; only the first term then remains, which agrees with (2′).

Moreover

$$\underset{cR=\infty}{Lim} \frac{H_0^{(2)}(cR)}{H_1^{(2)}(cR)} = -i. \quad ^{1})$$

It appears from the accompanying graphs [2]) of the module and argument of $\frac{H_0^{(2)}(cR)}{H_1^{(2)}(cR)}$ that this limiting value is practically reached at

$$\left.\begin{aligned} |cR| &= k.R = 10 \\ |c| &= k = \frac{2\pi\sqrt{2}}{\lambda} \text{ (cf. 8′)} \end{aligned}\right| \quad \ldots\ldots \quad (12)$$

The condition $|cR| \geqq 10$ means, that the radius of the cylinder must be about equal to or larger than the wave-length. If R is small compared with λ the second part of the frictional couple is negligible. For $|cR| \geqq 10$ the 2nd term on the right-hand side of (10) becomes

$$-aci\, e^{ipt} = -ak\, e^{i\left(pt+\frac{\pi}{4}\right)} \quad \left(\text{since } c = k\, e^{-\frac{i\pi}{4}}\right)$$

Hence equation (11) now becomes:

$$K = -4\pi\mu R^3 \omega - 2\pi\mu kR^3 \frac{d}{dt}\left(a\cos\left(pt+\frac{\pi}{4}\right)\right) \quad . \quad (13)$$

where

$$\omega = \frac{d}{dt}(a\cos pt).$$

The frictional couple thus divides into two parts, one which does not contain the density of the liquid and another, in which it occurs and which therefore refers to the emission of waves. In the transition to the limit of uniform rotation the first part only remains.

In the discussion of the 2nd part of the frictional moment the quantity $k = \sqrt{\frac{p\varrho}{\mu}}$ is an important factor. If we take a time of oscillation of 2π seconds, so that $p = 1$, we have $k = \sqrt{\frac{\varrho}{\mu}}$.

This gives the following values for k.

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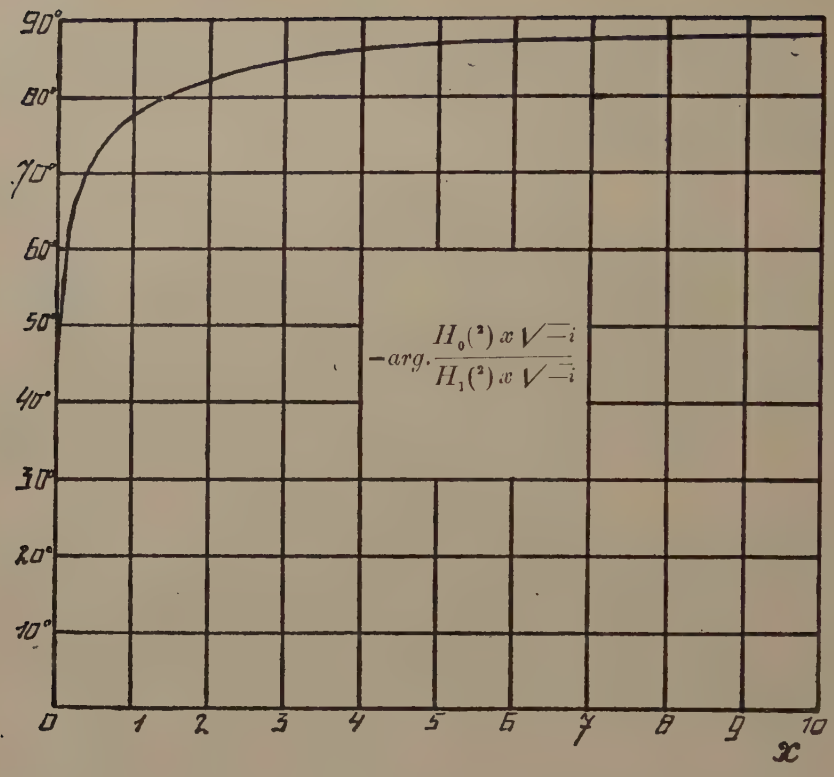
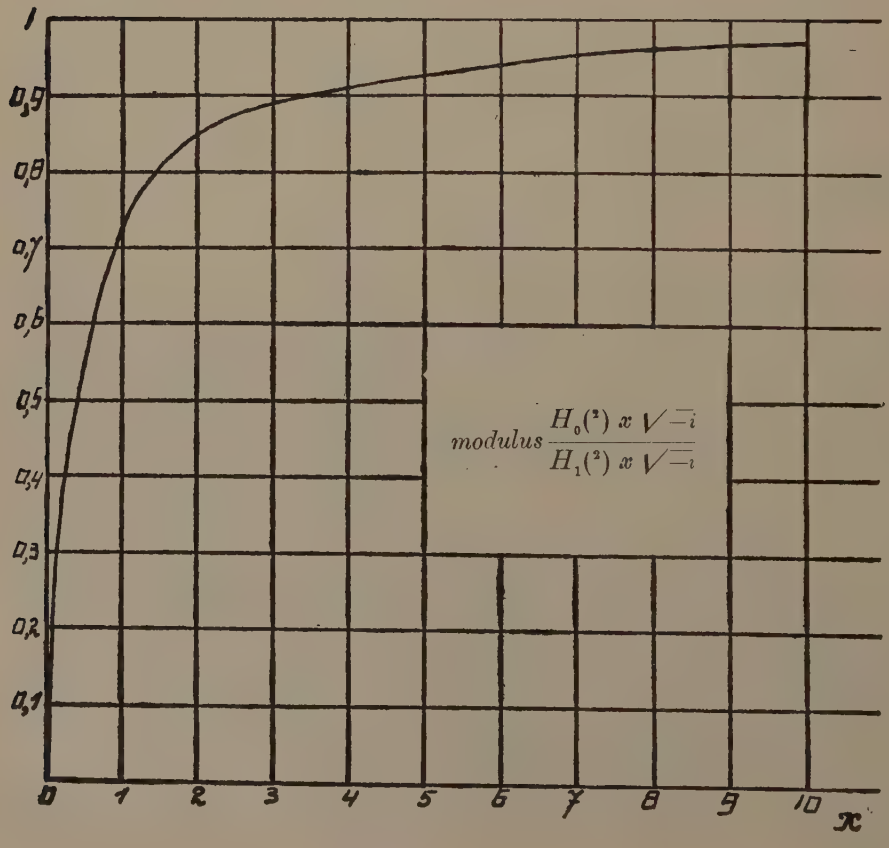
[1]) Comp. J. u. E. l. c.

[2]) Tables for $H_0^{(1)}$ and $H_0^{(2)}$ will be found J. u. E. p. 139, 140.


90°
80°
70°
60°
50°
40°
30°
20°
10°
0 1 2 3 4 5 6 7 8 9 10
x
$-arg.\frac{H_0^{(2)} x\sqrt{-i}}{H_1^{(2)} x\sqrt{-i}}$


1
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0 1 2 3 4 5 6 7 8 9 10
x
$modulus\frac{H_0^{(2)} x\sqrt{-i}}{H_1^{(2)} x\sqrt{-i}}$

	ϱ	μ	$k = \sqrt{\frac{\varrho}{\mu}}\ (p = 1)$.
Water 16°	1	0.011	9.5
Atm. air 0°	0.0013	0.000171	2.8
Air 0.01 atm. [1])			0.28
Air 0.001 atm. [1])			0.09
Hydrogen 1 atm. 0°	0.0000898	0.000085	1

From this table it appears that, except for dilute gases, R has to be relatively small in order that the 2nd part may be neglected with respect to the first. For instance for atmospheric air with $R = 0.5$ c.m. $kR = 1.4$ and $\left|\frac{H_0^{(2)}(cR)}{H_1^{(2)}(cR)}\right| = 0.80$, so that the amplitude of the 2nd term of the frictional couple is still 56 % of that of the first (see equation (11)), every thing calculated for a time of oscillation of 2π seconds.

There is a further special limiting case of equation (13), which is of some interest. Let R become infinite, and let a at the same time disappear, in such a manner that Ra converges to a finite limit b. We thus approach the one-dimensional problem of the oscillation of an unlimited flat plate in its own plane in an infinitely extended liquid. The frictional force per unit of surface is found from (13) to be

$$F = -\mu\, k \frac{d}{dt}\left(b \cos\left(pt + \frac{\pi}{4}\right)\right) \quad . \quad . \quad . \quad . \quad (14)$$

a formula which is well-known from hydrodynamics [2]). A term analogous to $-4\pi\mu R^2 \omega$ does not occur in the one-dimensional problem, the reason evidently being that with a uniform translation of the plate a condition of equilibrium does not arise, until the whole liquid away to infinity proceeds with the velocity of the plate.

Finally it is of importance to ascertain for what frequency the amplitude of the forced vibration becomes a maximum, in other words to what frequency the system cylinder-liquid resounds, if the cylinder is urged back to the position of equilibrium by a quasi-elastic force.

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[1]) At these pressures μ has not become much smaller. Comp. KUNDT u. WARBURG. Pogg. Ann. 1875 Band CLV.

[2]) Comp. LAMB. Hydrodynamics, 3rd edition 1905, p. 559.

The differential equation for the forced oscillation in complex notation is as follows:

$$\theta \frac{d^2\alpha}{dt^2} + L\frac{d\alpha}{dt} + M\alpha = Ee^{ipt} \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Here in our case L is a complex quantity $L = L' + iL''$, where

$$L' = (4\pi\mu R^3 + \sqrt{2}\,\pi\mu k R^3)$$
$$L'' = \sqrt{2}\,\pi\mu k R^3.$$

If we only concern ourselves with the particular solution of (15) which gives the forced oscillation, we can also write (15) in the form:

$$\left(\theta + \frac{L''}{p}\right)\frac{d^2\alpha}{dt^2} + L'\frac{d\alpha}{dt} + M\alpha = Ee^{ipt}. \quad . \quad . \quad . \quad . \quad (16)$$

We see therefore that in consequence of the motion of the liquid an apparent increase of the moment of inertia arises.

Putting

$$\theta + \frac{L''}{p} = \theta'$$

the particular solution of (16) becomes:

$$\alpha = \frac{E}{\sqrt{(M - \theta' p^2)^2 + L'^2 p^2}} e^{i(pt - \varphi)}$$

in which the phase-angle φ is determined by the constants of the differential equation.

Resonance occurs for $M - \theta' p^2 = 0$

or

$$\theta p^2 + L'' p - M = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Now L'' is proportional to k and $k = \sqrt{\frac{p\varrho}{\mu}}$, so that we may conveniently write $L'' = Np^{\frac{1}{2}}$, N being a constant.

(17) is now replaced by

$$\theta p^2 + Np^{1\frac{1}{2}} - M = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

This equation which is bi-quadratic in $\sqrt{p}$ determines the frequencies to which the system resounds. On closer examination there appears to be but one resonance-frequency. Naturally we are only concerned with the real roots p of equation (18). There are found to be two of such, one for which $\sqrt{p}$ is positive, and another for which $\sqrt{p}$ is negative. Now it follows from our calculation that we have assumed $\sqrt{p}$, which occurs in k to be essentially positive. For if we substitute a negative value for $\sqrt{p}$ in our equations, we obtain a system of waves which moves from infinity towards the cylinder.

But the amplitude of this system is infinite at infinity, so that our first boundary-condition would not be satisfied.

We may also choose our boundary-conditions differently. We may for instance imagine the liquid limited on the outside by a second cylinder co-axial with the first and at rest. It is then advisable to write the general solution of equation (4) in the following form

$$u = \frac{1}{r}\{C\,H_1^{(2)}(cr) + D\,H_1^{(2)}(cr)\} \quad . \quad . \quad . \quad . \quad . \quad (19)$$

At a sufficient distance from the axis of the cylinders two systems of waves then arise, one of which is propagated outwards and the other inwards. At the surface of the exterior cylinder we obtain reflection with reversal of phase, so that the liquid there is at rest. For the determination of the integration-constants C and D we obtain comparatively complicated relations which may be omitted here as they do not yield anything of further interest.

The problem of the free oscillation does not now give any further special difficulties.

We must now seek a solution of equation (1) of the form

$$a_r = f_{(r)}\, e^{-k't} \cos(k''t - \varphi(r)),$$

which for $r = R$ becomes $a_R = a\, e^{-k't} \cos k''t$. Again we may write $a = u\, e^{nt}$, where $n = -k' + ik''$.

The same method of solution may now be followed. Instead of (7) we obtain:

$$a_r = \frac{aR}{H_1^{(2)}(c'R)} \frac{H_1^{(2)}(c'r)}{r} e^{nt}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where $c' = \sqrt{-\frac{n\varrho}{\mu}}$, if for c' the root with the negative imaginary part is chosen. Hence

$$\left[\frac{da_r}{dr}\right]_R = -\frac{2a}{R} e^{nt} + ac' \frac{H_0^{(2)}(c'R)}{H_1^{(2)}(c'R)} e^{nt}. \quad . \quad . \quad . \quad . \quad (21)$$

$$\lim_{|c'R| = \infty} \frac{H_0^{(2)}(c'R)}{H_1^{(2)}(c'R)} = -i$$

Therefore:

$$\left[\frac{da_r}{dr}\right]_R = -\frac{2a}{R} e^{nt} - a\sqrt{\frac{n\varrho}{\mu}}\, e^{nt}, \quad . \quad . \quad . \quad . \quad (22)$$

if for $\sqrt{\frac{n\varrho}{\mu}}$, we take the root with the positive real term.

The frictional moment now becomes:

$$2\pi\mu R^3\left[\frac{d\dot{\alpha}}{dr}\right]_R = -2\pi\mu R^3\left[\frac{2}{R}+\sqrt{\frac{n\varrho}{\mu}}\right]\dot{\alpha}_R.$$

The differential equation for the free vibration is:

$$K\frac{d^2\alpha}{dt^2}+L\frac{d\alpha}{dt}+M\alpha=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

giving for the natural frequencies of the system the equation

$$Kn^2+Ln+M=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

The quantity L here contains $\sqrt{n}$.

If we put $L=P+Q\sqrt{n}$, where

$$P=4\pi\mu R^3 \text{ and } Q=2\pi\mu RR^2\sqrt{\frac{\varrho}{\mu}},$$

(24) assumes the form:

$$Kn^2+(P+Q\sqrt{n})n+M=0 \quad . \quad . \quad . \quad . \quad . \quad (25)$$

Equation (25) is bi-quadratic in $z=\sqrt{n}$. On further examination it is found to have 2 complex roots z in the right hand portion of the complex plane and 2 in the left portion, only the former of which we can use (comp. equation (22)); hence the system has but one natural frequency. Further $z^2=n$ is found to contain a negative real term, as indeed could not be expected otherwise.

Chemistry. — *"Investigations on* PASTEUR'S *Principle concerning the Relation between Molecular and Crystallonomical Dissymmetry*: **V.** *Optically active complex-salts of Iridium-Trioxalic Acid"*. By Prof. F. M. JAEGER.

(Communicated in the meeting of June 29, 1918).

§ **1.** A short time ago I published [1]) some data about the properties of *racemic Potassium-Iridium-Oxalate*: $\{K_3\ Ir\ (C_2\ O_4)_3\} + + 4\frac{1}{2}\ H_2O$ [2]), and on that occasion I announced experiments undertaken with the aim of splitting this compound into its optical antipodes. It was our purpose to gain in this way the necessary information to enable us to indicate the correct configuration in space of these optically active complex ions, in comparing it with that attributed to the corresponding *rhodium*-derivatives, in consequence of the arguments brought forward on that occasion. At the same time I hoped to investigate in this way, what influence the substitution of the central *rhodium*-atom in these complex ions by the homologous *iridium*-atom appeared to have upon the magnitude and the specific character of the optical rotation and its remarkable dispersion. It may be considered of importance, of course, to know the relation existing between the two functions just mentioned, especially in connection with our former studies on the analogously constituted complex salts of *cobalt* and *rhodium* combined with three molecules of *ethylenediamine*, where the problem arose as to the true configurative relations between the salts of these homologous metals of the eighth group of the periodic system, when rotating the plane of polarisation in the same direction [3]).

In the following the fission-experiments mentioned and the results obtained by them are recorded in details. Thus for the first time the possibility of a "partial" asymmetry [4]) has been proved, in the case of *iridium* as the central atom; the series of the metals showing

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1) F. M. JAEGER, Proceed. R. Acad. Amsterdam. **20**. 263. (1917).

2) C. GIALDINI, Rend. Acad. d. Linc., *Roma*, (5*a*), **16**. II. 551. (1907); Proceed. Acad. Amsterdam, loco cit. p. 278.

3) F. M. JAEGER, Proceed. R. Acad. Amsterdam, **17**. 49. (1915); **20**. 244. (1917); conf. Zeits. f. Kryst. u. Miner. **55**. 209. (1915).

4) F. M. JAEGER, *Lectures on the Principle of Symmetry, Amsterdam*, (1917), p. 235.

this phenomenon being herewith extended to *chromium, iron, cobalt, platinum, rhodium,* and *iridium.* With respect to the dispersion of some of these salts, we hope yet to furnish some new data in the near future.

§ **2.** The required *racemic Potassium-Iridium-Oxalate*: $K_3\{Ir(C_2O_4)\} + 4\frac{1}{2}H_2O$ was obtained in the following way. A 3 % solution of pure, hydrated *iridiumchloride* of commerce (HERAEUS) is treated by a solution of *potassiumhydroxide* in excess. A dirty brownish precipitate is formed, which dissolves in the excess of KOH to form *potassium-iridiate.* The alkaline solution is heated, and then some *perhydrol* (30 % H_2O_2) added: the colour changes to dark blue, and the principal part of the *iridium* precipitates as $Ir(OH)_4$, Another part of it remains in the solution as a colloïdal suspension of great stability, not being precipitated or coagulated from it, even after addition of electrolytes. These solutions are therefore better evaporated, and the residue transformed into *ammonium-chloro-iridiate* to be used afterwards in other experiments.

The blue precipitate is washed by decantation with water slightly acidified by means of *oxalic acid*; the filtrates and washings are also later converted into the mentioned compound. When the removed liquid gets colourless, the decantation may be considered complete, and the precipitate is brought into a round bottom flask, the superfluous liquid removed after some hours, standing, and a hot, concentrated solution of *oxalic acid* added. The contents of the vessel are boiled under a reflux-condenser during 30 or 40 hours; a part of the *oxalic acid* is thereby decomposed, and the tetravalent *iridium* reduced to trivalent according to the equation:

$$2Ir(OH)_4 + C_2O_4H_2 = 2Ir(OH)_3 + 2H_2O + 2CO_2,$$

while *iridium-trioxalic acid* is then formed from the derivative of the trivalent *iridium,* conforming to the equation:

$$2Ir(OH)_3 + 6C_2O_4H_2 = 2\{Ir(C_2O_4)_3\}H_3 + 6H_2O.$$

The gold-yellow solution finally obtained is filtered, and almost perfectly neutralised by means of $KHCO_3$; it is then concentrated on the waterbath, and the successive fractions of the crystals formed are separately collected. Almost pure *potassium-oxalate* is first deposited, and afterwards, besides this, the orange crystals of the salt required, which is very soluble. These crystals have to be separated mechanically, and they are afterwards recrystallised for purification [1]).

The racemic compound crystallises in pale orange-coloured crystals,

[1]) Dr. J. KAHN has aided most effectively in the preparation of a part of this racemic compound, and in the troublesome working up of the *iridium*-residues.

which have already been investigated and described in a former paper [1]). They are triclinic-pinacoidal, and completely isomorphous with the corresponding racemic *rhodium*-salt, so that the direct isomorphous substitution of the metals *Rho* and *Ir*, also in their complex salts, has been hereby definitely proved. As we shall see, this proof has now also been given in the case of the *optically-active components* of such complex salts.

§ 3. *Fission of the racemic Potassium-Iridium-Oxalate* ($+4^1/_2 H_2O$) *into its optically-active components.*

27,5 Grams of pure *strychnine-nitrate* are dissolved in 1300 ccm. boiling water; then a solution of 15,5 grams of the racemic salt in 250 ccs water of 60° C. is rapidly poured into the boiling solution under perpetual stirring. The flask with the golden yellow liquid is allowed to cool slowly for twelve hours to room-temperature. The deposited, highly yellowish coloured, felty-like crystals are sharply sucked off at the water-pump, washed with some strong alcohol, afterwards with some ligroine, and dried at room-temperature in an air-current. The mother-liquid is evaporated on the waterbath to about $^2/_3$ of its original volume; on cooling highly yellow, needle-shaped crystals are again deposited, which are treated in the same way. While the first fraction, however, represents the *strychnine*-salt of the *dextro*gyratory component, — the *laevo*-gyrate antipode was immediately obtained from the second precipitate. On further evaporation of the filtrate, some paler coloured fractions are consecutively obtained, all of which give the *laevo*-gyratory *potassium*-salt. The sixth and the seventh fraction finally consisted of pure *strychnine*, accompanied by some of its *nitrate*, while in the last fractions crystals of the free, *racemic potassium*-salt together with some of the laevo-salt, and also some potassium-nitrate, appeared. The rotation of this last fraction as a whole, after removing the potassium-nitrate, was negative, amounting only to about $^1/_7$ of the rotation of the pure laevogyrate salt, so that a considerable amount of racemic salt is evidently admixed. Probably a partial hydrolysis during the repeated evaporations has taken place, so that the free potassiumsalt accumulates in the last fractions.

The *strychnine*-salt of the *dextro*gyratory component has the formula: $\{Ir(C_2O_4)_3\}_2(C_{21}H_{22}N_2O_2)_3 + 3\frac{1}{2}H_2O$; it appears as pale yellow, very fine needles. For a series of wave-lengths the rotation of this strongly active salt was determined; the solution used contained 0,4763 grams of the hydrated salt in 100 ccs. of the liquid.

[1]) F. M. Jaeger, Proceed, R. Acad. Amsterdam, **20**, 278, (1917).

The following data were found:

Rotation-dispersion of Strychnine-*d*-Iridium-Oxalate ($+ 3\frac{1}{2} H_2O$).		
Wave-length in A. U.:	*Observed Rotation:*	*Molecular Rotation:*
5105	+ 1°.02	+ 20997°
5260	0.86	17703
5430	0.65	13379
5610	0.38	7822
5800	0.27	5558
6020	0.21	4323
6260	0.17	3499
6530	0.15[5]	2676

In the same way the composition of the corresponding *strychnine*-salt of the *laevo*gyrate component appeared to be: $\{Ir(C_2O_4)_3\}C_{21}H_{22}N_2O_2)_3 + 3H_2O$. This salt too crystallises in needles, somewhat thicker than those of the first. The substance is strongly *laevo*gyratory, and its dispersion is smaller than in the case of the other salt, as may be seen from the following data, and the graphic representation in fig. 1:

Rotation-dispersion of Strychnine-*l*-Iridium-Oxalate ($+ 3 H_2O$).		
Wave-length in A. U.:	*Observed Rotation:*	*Molecular Rotation:*
5105	— 0°.33	— 17236°
5260	0.28	14624
5430	0.24	12535
5610	0.19	9994
5800	0.15	7835
6020	0.12[5]	6057
6260	0.09	4701
6530	0.08	4178

This solution contained 0,1886 grams of substance in 100 grams of the liquid.

It is remarkable that the laevogyrate *strychnine*-salt has a somewhat greater molecular rotation than the corresponding *potassium*-salt itself; the dextrogyrate *strychnine*-salt rotates more strongly than the free *potassium*-salt.

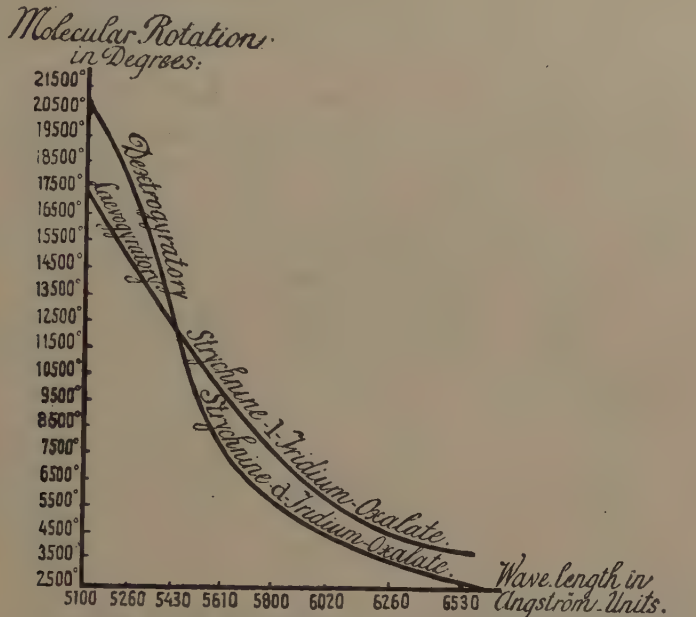


Fig. 1. *Molecular Rotation Dispersion of Strychnine-d-Iridium--Oxalate* ($+3\frac{1}{2}H_2O$) *and of Strychnine-l-Iridium-Oxalate* ($+3H_2O$).

§ 4. The different fractions were mixed with about six times their weight of finely pulverized *potassium-iodide*, and then ground together in a mortar, some cold water being added to the mixture. When all potassium-iodide has just been dissolved, the yellow liquid is sharply sucked off from the white precipitate, this last washed with a very small quantity of cold water, and the yellow filtrate precipitated by the addition of an excess of 95 % alcohol. A yellow deposit is formed, which is sucked off on the BUCHNER-filter, washed with alcohol, and recrystallised from water. On heating on the waterbath the solution does not autoracemise notably. By slow crystallisation at roomtemperature, beautiful trigonally-shaped, orange crystals are formed, which are dried between filterpaper. They can grow in their mother-liquid to considerable size. The optically-active components are extremely soluble, more than the very soluble racemic compound; on this account the crystallisation of the active components was executed in smaller and somewhat deeper crystallisation-dishes.

§ 5. The rotation-dispersion of these optically-active *iridium*-salts was measured in the same way as formerly by means of a great polarimeter of SCHMIDT and HAENSCH, with threefold field, and equipped with a monochromator. The tube was always 20 cm. long, and determinations were made for a whole series of wave-lengths. Even in thin layers of the liquid the spectral region of the transmitted light appeared to be appreciably limited by absorption, also in the case of not very concentrated solutions.

Waves larger than 6850 A.U. were never transmitted to a sufficient degree, while even in a solution of 1 % no exact determinations could be made for wave-lengths smaller than 5300 A.U. To investigate the shape of the dispersion-curve also for shorter wavelengths, it was therefore necessary to use very dilute solutions, of 0,2 % and 0,1 % or less. We have used four such solutions for this purpose, containing respectively one grammolecule of the hydrated salt in 14,57 Liters (*a*) of the solution, in 57,73 Liters (*b*), in 228,86 Liters (*c*), and in 413,7 Liters (*d*).

In the following table the mean values are taken into account, and the molecular rotations calculated from them; in fig. 2 these results are moreover graphically plotted, in their relation to the light used:

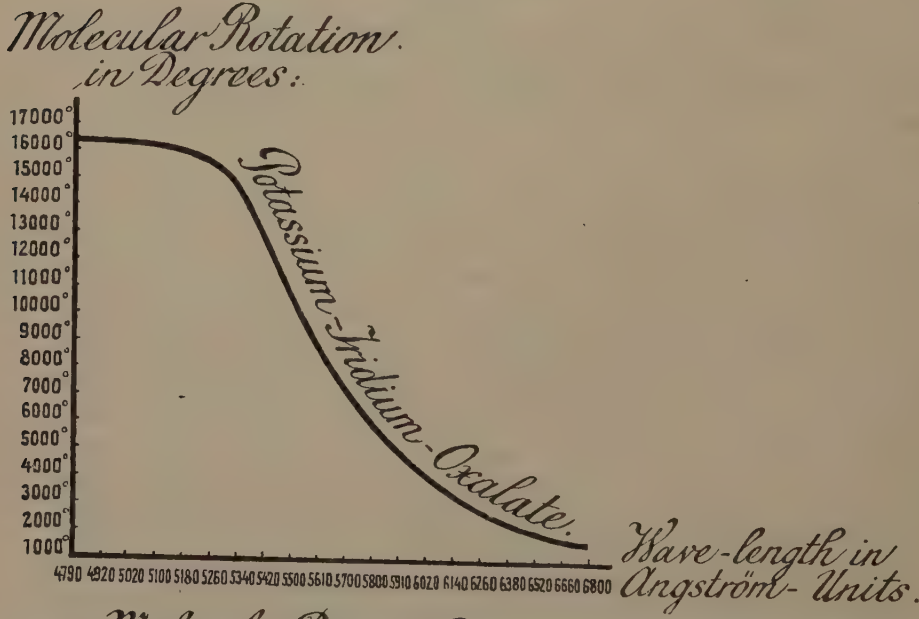


Fig. 2. *Molecular Rotation-Dispersion of the Optically active Potassium-Iridium-Oxalates.*

The values obtained with the different solutions agreed very well

together. In the table are therefore quoted those values which approached nearest to the curve of the mean values. The dispersion-curve shows a tendency to get more and more horizontal for wave-lengths beneath 5100 A.U.

ROTATION-DISPERSION OF DEXTROGYRATE POTASSIUM-IRIDIUM-OXALATE ($+ 1\,H_2O$).

Wave-length in A. U.:	*Observed Rotation in Degrees:*	*Molecular Rotation in Degrees:*
4790	+ 0.°79 (*d*)	+ 16340°
4920	0.78⁵ (*d*)	16237
5020	0.78 (*d*)	16134
5100	0.78 (*d*)	16134
5180	0.77 (*d*)	15927
5260	0.75 (*d*)	15514
5340	1.28 (*c*)	14647
5420	4.36 (*b*)	12586
5510	14.42 (*a*)	10508
5610	11.94 *id.*	8699
5700	9.88 *id.*	7198
5800	8.17 *id.*	5952
5910	6.86 *id.*	4998
6020	5.49 *id.*	4000
6140	4.73 *id.*	3446
6260	3.86 *id.*	2813
6380	3.32 *id.*	2446
6520	2.61 *id.*	1901
6660	2.33 *id.*	1698
6800	2.10 *id.*	1530

Although the dispersion of these orange-coloured solutions is extraordinarily strong, the slope of the curve is quite different from that found in the case of the corresponding *rhodium*-salt. This fact proves the preponderant influence of the special nature of the

central metal-atom on the specific light-absorption (colour) of these salts and on the whole character of the rotation-dispersion.

The yellow crystals obtained on evaporating the original mother-liquid of the *strychnine*-salts to $^2/_3$ or $^1/_2$ of its volume, gave after treatment with potassium-iodide a fraction which appeared to be the *pure laevogyrate* salt. The following measurements, made with a solution containing one grammolecule of the hydrated salt in 42,97 Liters of the liquid, may make this clear:

ROTATION-DISPERSION OF THE LAEVOGYRATE POTASSIUM-IRIDIUM-OXALATE ($+ 1H_2O$).

Wave-length in A. U.:	*Observed Rotation in Degrees:*	*Molecular Rotation in Degrees:*
5340	— 6.66°	— 14287°
5430	5.72	12289
5520	4.89	10506
5610	3.86	8293
5700	3.26	7004
5800	2.70	5801
5910	2.28	4898
6020	1.95	4189
6140	1.63	3502
6260	1.35	2900
6340	1.07	2299
6520	0.88	1891
6660	0.74	1590
6800	0.70	1504

A comparison of the rotations for the same wave-lengths in the case of the corresponding *rhodium*-salt with the here described

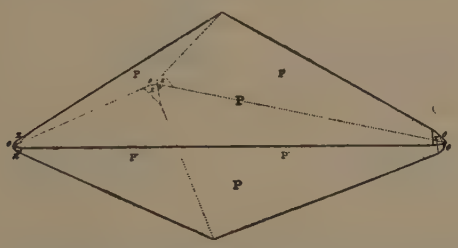
Salt:	*Molecular Rotation:*	*Atomic Volun of the metal*
$K_3\{Rho(C_2O_4)_3\} + H_2O$.	$M_{4930} = 14200°$; $M_{5800} = 790°$; $M_{5970} = 0°$; $M_{6660} = -1215°$.	8 50
$K_3\{Ir(C_2O_4)_3\} + H_2O$.	$M_{4930} = 16230°$; $M_{5800} = 5952°$; $M_{5970} = 4500°$; $M_{6660} = +1698°$.	8.61

iridium-salts, teaches us, that the rotation of the *iridium*-salt is always appreciably *greater* than that of the *rhodium*-salt, although the atomic volume of *iridium* differs only slightly from that of *rhodium*, and even exceeds it by a small amount.

If we were able to demonstrate later, that for $\{Ir(Aeïne)_3\}I_3$ the rotations are smaller than those of the corresponding *rhodium*-salt, then we should have proved that the influence of the atomic volume on the magnitude of the rotation, may be in this or in the opposite direction, according to there being either basic or acid substituents attached to the central-atom.

§ 6. Dextrogyratory Potassium-Iridium-Oxalate: $K_3\{Ir(C_2O_4)_3\}+1H_2O$.

Beautiful, rather large, orange-coloured, and very lustrous crystals, which are commonly regularly developed in the shape of flattened, triangular bipyramids. They are well built and geometrically easily determinable, allowing very exact measurements. The deviations of the angular values from those found with the corresponding *rhodium*-



Dextrogyratory Potasium-Iridium-Oxalate.
Fig. 3.

salt are more appreciable than ordinarily stated in the case of rigorously isomorphous crystals.

The symmetry of the two series of crystals is however exactly the same, and their form-analogy is sufficiently great, to consider the optically-active salts of the two series as quite isomorphous, also with respect to the doubtless isomorphy between the racemic salts of the *rhodium*-, and the *iridium*-series. The more deviating values of the angles and axial parameters are probably connected with the rather great difference of atomic weight of the metal-atoms. Analysis teaches us, that also these optically-active salts crystallise with only one molecule of water.

Trigonal-trapezohedral.

$a : c = 1 : 0{,}9520$. (Bravais); $a = 100°20'$. (Miller).

Forms observed: $P = \{11\bar{2}2\}\,[52\bar{1}]$, as positive trigonal bipyramid,

predominant and yielding good reflexes; $o = \{10\bar{1}1\}$ [100], positive rhombohedron of the first kind, well reflecting, but in most cases only with rather small facets; $x = \{1\bar{1}01\}$ [$\bar{2}12$], a negative rhombohedron of the first kind, commonly much broader than o, somewhat less lustrous; $y = \{2\bar{1}\bar{1}1\}$ [$4\bar{2}1$], a negative trigonal bipyramid, about as large as x, but much smaller than P, commonly yielding good mirror-images; $r = \{1\bar{1}02\}$, as a narrow obtusion of the edges of the rhombohedron o, ordinarily absent, but in the other case very lustrous. Sometimes a very narrow and rudimentarily developed prism $m = \{11\bar{2}0\}$ was observed, truncating the basal edges of P. The crystals are mostly very regularly developed as flat trigonal bipyramids; but occasionally more or less deformed, table-shaped individuals are met with, showing the same combination of forms. The faces of P are often striated parallel to the edges $P : o$. (Fig. 3). Also crystals are found, where o is about twice as large as P; in this case the striation on P was observed in all cases.

Finally we met with individuals showing only P and o in about equal size, P having its characteristic striation; besides them also y was found occasionally, but very small and subordinate, especially in the case of the dextrogyrate component.

Angular Values:	*Observed*:	*Calculated*:
$P : P'' = (11\bar{2}2) : (1\bar{2}12) =$*	73° 20′	—
$P : P' = (11\bar{2}2) : (11\bar{2}\bar{2}) =$	92 49	92° 49′
$P : o = (11\bar{2}2) : (10\bar{1}1) =$	21 40	21 43
$x : o = (1\bar{1}01) : (10\bar{1}1) =$	43 28	43 26
$x : y = (1\bar{1}01) : (2\bar{1}\bar{1}1) =$	28 20	28 21
$y : o = (2\bar{1}\bar{1}1) : (10\bar{1}1) =$	28 24	28 21
$P : o = (1\bar{2}12) : (10\bar{1}1) =$	60 48	60 50½
$o : o = (10\bar{1}1) : (0\bar{1}11) =$	79 30	79 40
$o : r = (10\bar{1}1) : (1\bar{1}02) =$	39 43	39 50
$m : P = (11\bar{2}0) : (11\bar{2}2) =$	46 30	46 25

No distinct cleavage was observed.

Optically uniaxial, without noticeable circular polarisation. The character of the birefringence is negative.

The specific gravity of the crystals at 20° C. was: 2,734; the molecular volume is therefore: 217,77, and the topical parameters are: $\chi : \omega = 7{,}0618 : 6.7230$, if calculated with respect to hexagonal axes, and $\chi = \psi = \omega = 6{,}1321$, with respect to rhombohedral axes.

§ 7. The crystals of the laevogyrate antipode ordinarily showed only the bipyramid *P*, which must be considered as a *left*handed bipyramid here, because all phenomena are in agreement in this case with PASTEUR's law, as is proved beyond doubt by the hemihedral symmetry of the crystals. Therefore to this bipyramid must be attributed the symbol $\{2\,\bar{1}\,1\,2\}$ $[5\bar{1}2]$; besides the forms *o*, *x*, and *y*, *y* having the symbol $\{1121\}$ $[41\bar{2}]$, appear subordinately here. Because *o* and *x* were in most crystals about equally large, and could not be discerned in any other way, the external habit of these lefthanded crystals was not different from that of dextrogyrate salt, the latter being brought into the same position as the lefthanded by a rotation through 60° round the trigonal axis, with the only difference, that the forms *x* and *o* are thereby interchanged. However, if *x* and *o* are of unequal size, the occurrence of mirror-images could be seen immediately in the crystals. The zonal relations may be made clear by the subsequent stereographical projections (Fig. 4). Just as in the case of oppositely rotating *rhodium*-salts, a non-superposable hemihedrism accompanies here the contrary power of rotation.

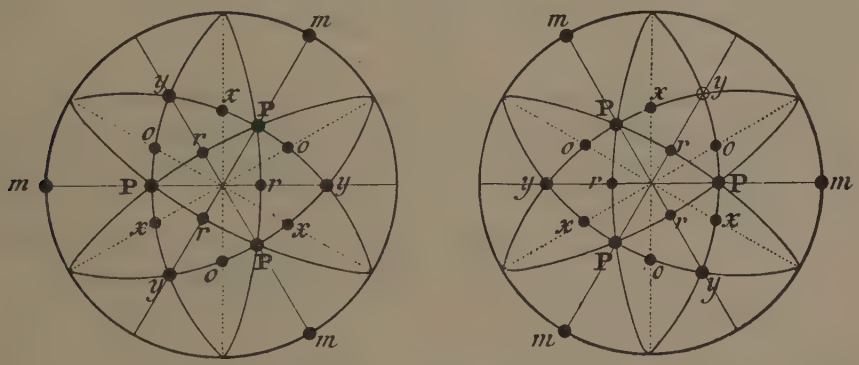


Fig. 4. *Stereographical Projection of the Crystalforms of d- and l-Potassium-Iridium-Oxalate (only the top-ends of the crystals).*

§ 8. The specific gravities of the formerly investigated *rhodium*-salts, were determined at $d_{4^0}^{20^0} = 2{,}171$ for the racemic compound $(4\frac{1}{2}\ H_2O)$, corresponding to a molecular volume of: 260,34; and at $d_{4^0}^{20} = 2{,}255$ for each of the optically-active salts $(+\ 1\,H_2O)$, which corresponds to a molecular volume of 222,70. From this the topical axes of these salts are calculated at:

$\chi : \psi : \omega = 6{,}8980 : 6{,}4274 : 6{,}6306$, for the racemic *rhodium*-salt, and $\chi : \omega = 7{,}2660 : 6{,}4944$, for the optically-active salts, with respect to hexagonal axes, and $\chi = \psi = \omega = 6{,}1856$, with respect to rhombohedral axes.

Comparison with the corresponding parameters of the here studied *iridium*-salts [1]):

Salt:	*Topical Parameters:*
racemic $K_3\{Rho(C_2O_4)_3\}, 4\frac{1}{2}H_2O$.	$\chi : \psi : \omega = 6{,}8980 : 6{,}4274 : 6{,}6306$.
racemic $K_3\{Ir(C_2O_4)_3\}, 4\frac{1}{2}H_2O$.	$\chi : \psi : \omega = 6{,}7454 : 6{,}2626 : 6{,}5162$.
optically-active $K_3\{Rho(C_2O_4)_3\}, H_2O$.	$\chi : \omega = 7{,}2660 : 6{,}4944$; $\chi' = 6{,}1856$.
optically-active $K_3\{Ir(C_2O_4)_3\}, H_2O$.	$\chi : \omega = 7{,}0618 : 6{,}7230$; $\chi' = 6{,}1321$.

teaches us, that the substitution of the central *Rho*-atom in the complex oxalate by the isomorphous *Ir*-atom, produces a diminution of the topical parameter ω in the case of the racemic salts, but a slight increase, in the case of the optically active antipodes, although the values for χ and χ' are in this case smaller with the corresponding *Rho*-salt.

In the same way as in the case of the previously described *rhodium-oxalate*, all phenomena observed in the fission of *potassium-iridium-oxalate* are really in full agreement with the sense of PASTEUR'S *law*.

Laboratory for Inorganic and Physical Chemistry of the University.

Groningen, June 1918.

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[1]) The specific gravity of *racemic* $K_3\{Ir(C_2O_4)_3\} + 4\frac{1}{2}H_2O$ was at 18° C. determined at: $d_4^{18} = 2{,}688$; the molecular volume is thus: 243,82.

Chemistry. — *"Investigations on* PASTEUR'S *Principle concerning the Relation between Molecular and Crystallonomical Dissymmetry*: **VI.** *On the Fission of Potassium-Rhodium-Malonate into Its Optically-active Components."* By Prof. F. M. JAEGER and WILLIAM THOMAS. B. Sc.

(Communicated in the meeting of June 29, 1818).

1. Some time ago one of us[1]) described the crystalform of *racemic Potassium-Rhodium-Malonate*: $K_3\{Rho(C_3H_2O_4)_3\} + 3H_2O$, and hinted at the possibility of separating this salt into its optically-active components. In the following we are now able to describe the results of the respective experiments, which have led to a positive result, and to give a review of the highly remarkable rotation-dispersion of these new salts.

The racemic salt nesessary for these experiments was prepared in the following way. A 3 %-solution of pure $Na_3RhoCl_6 + 9H_2O$ was heated to 40° C, and then precipitated by means of a 10 % solution of caustic potash, so much of the base being added, that the liquid showed a feeble alkaline reaction. The precipitate is separated from the excess of potash as well as possible by repeated decantation in high cylindrical vessels; it settles down extremely slowly, so that this operation takes much time. Then the precipitate is brought into a round bottom distilling-flask and heated under a reflux-cooler some forty hours with a solution of the calculated amount of *potassium-bimalonate*: $KHC_3H_2O_4$, and some free *malonic acid*, until the precipitate no longer diminishes in quantity. The red coloured liquid is then filtered, and concentrated on the water-bath: on slow evaporation at room-temperature there soon appear red flat crystals of the complex malonate, which are once more recrystallised from water for purification. The residue in the flask is again changed into the complex *sodium-rhodium-chloride*: $Na_3RhoCl_6 + 9H_2O$ in the usual way, and afterwards precipitated as described in the above.

§ **2.** After a series of attempts we succeeded in separating this salt, which crystallises in beautiful monoclinic crystals[2]), into its optically-active components by the aid of its *cinchonine*-salt.

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[1]) F. M. JAEGER, Proceed. Kon. Acad. Amsterdam, **20.** 276. (1917).

[2]) *loco citato*, p. 277.

For this purpose the *potassium*salt is first converted into the *barium*salt, by adding a strong solution of 3 molecules of *barium-chloride* to a concentrated solution of 2 molecules of the potassium-salt: a yellow precipitate is formed, which dissolves rather easily in hot water, but which can be almost completely precipitated from its aqueous solution by the addition of 97 % alcohol. This barium-salt was now dissolved in water at 50° C, and then a solution of one equivalent *cinchonine-sulphate* [1]), also heated to 50° C, was added to it. The solutions need not be too concentrated, because the *cinchonine-rhodium-malonate* will otherwise partly precipitate, as it is only sparingly soluble. The bariumsulphate formed is carefully sucked off, and by washing with water of 45° C. all the included yellow *cinchonine*-salt eliminated. On standing for 24 hours in a large crystallising-dish, the liquid begins to deposit beautiful, pale yellow and often in rosettes united needles of the *cinchonine*-salt of the *laevo*gyrate component, as will soon be shown. On repeated partial evaporation of the mother-liquid on the waterbath, the successive fractions were separately collected and investigated. The first three fractions appeared to contain the *left*handed component; the fourth fraction gave the almost pure *dextro*gyrate antipode, the fifth and sixth fractions the pure dextrogyrate component immediately. It is a remarkable fact that the *cinchonine-l-malonate* and the *cinchonine-d-malonate* are both *dextro*-gyratory, notwithstanding the very large rotation of opposite sign of the complex ions present therein. This peculiar behaviour was checked by us by a special control, namely by preparing the free *potassium*-salts again from the *cinchonine*-salts used in the polarimetric measurements. We could easily prove in this way, that the salts thus obtained, really represented the right and left antipodes. From the pure *laevo*gyrate *potassium*salt we once more prepared the corresponding *cinchonine*-salt by means of the *barium*-salt; the rotations determined with this especially prepared salt proved to be positive, and they agreed very well with those formerly found. We have also investigated the influence of the addition of three molecules of *cinchonine* to a solution of the optically-active *potassium*-salts, and the rotations found with these solutions were compared with those

[1]) Originally we tried to reach our purpose by means of the *strychnine*-salt, as in the case of the *rhodium-oxalate*. However, these experiments had no result, the *potassium*salt prepared from the carefully fractionated *strychnine*-salt by *potassium-iodide* being always optically-*in*active. It is difficult to say whether racemisation or partial racemism is the cause of this; but only after several failures we passed to the use of *cinchonine*.

of *cinchonine* itself: the observed rotations appeared to be practically identical with those of the *cinchonine-l-rhodium-malonate*, so that evidently the influence of the three molecules of *cinchonine* far outweighs that of the laevogyrate *rhodium-malonate-ion* itself.

The last fractions of the crystallisation-series of the *cinchonine*-salt finally gave pure *cinchonine*, a small amount of the dextrogyrate salt and a certain quantity of the racemic salt remaining in the last mother-liquids. Evidently also here the repeated evaporation on the waterbath, just as in the case of the corresponding *oxalate*, seems to cause a partial hydrolysis. Analysis taught us that the *cinchonine-d-rhodium-malonate* crystallises with $3\,H_2O$; the corresponding *cinchonine-l-rhodium-malonate* with $^1/_2\,H_2O$. This last mentioned salt could not be heated above 100° C, being less stable than the right-handed salt, it is rapidly decomposed with formation of a dirty brown powder.

For the rotation-dispersion of the *cinchonine*-salts we found the following values:

I. CINCHONINE-*d*-RHODIUM-MALONATE ($+3\,H_2O$).

Wave-length in A. U.:	Observed Rotation in Degrees:	Molecular Rotation in Degrees:
5105	+ 1,37°	+ 30010°
5260	1,23	26943
5420	1,14	24972
5610	1,07	23406
5800	0,99	21686
6020	0,94	20591
6260	0,88	19277
6520	0,84	18400

The solution investigated contained 0,3070 grams of the hydrated salt in 100 grams of the liquid.

The results obtained are plotted in the figure 1. It shows us, that *both* curves are situated *above* that of pure *cinchonine*, notwithstanding the fact, that one of them contains the strongly negatively rotating complex *rhodium-malonate*-ion; of a simple superposition of the optical activities there is therefore no question.

The transformation of the *cinchonine*-salts into the corresponding *potassium*-salts was carried out in the following way. The pure

II. Cinchonine-*l*-rhodium-malonate ($+ {}^1/_2 H_2O$).		
Wave-length in A.-U.:	Observed Rotation in Degrees:	Molecular Rotation in Degrees:
5105	$+ 0{,}65°$	+ 16617°
5260	0,61	15622
5420	0,57	14598
5610	0,52	13384
5800	0,45	11525
6020	0,40	10244
6260	0,36	9220
6520	0,32	8195

The solution used had 0,2538 grams of the hydrated salt in 100 grams of the liquid.

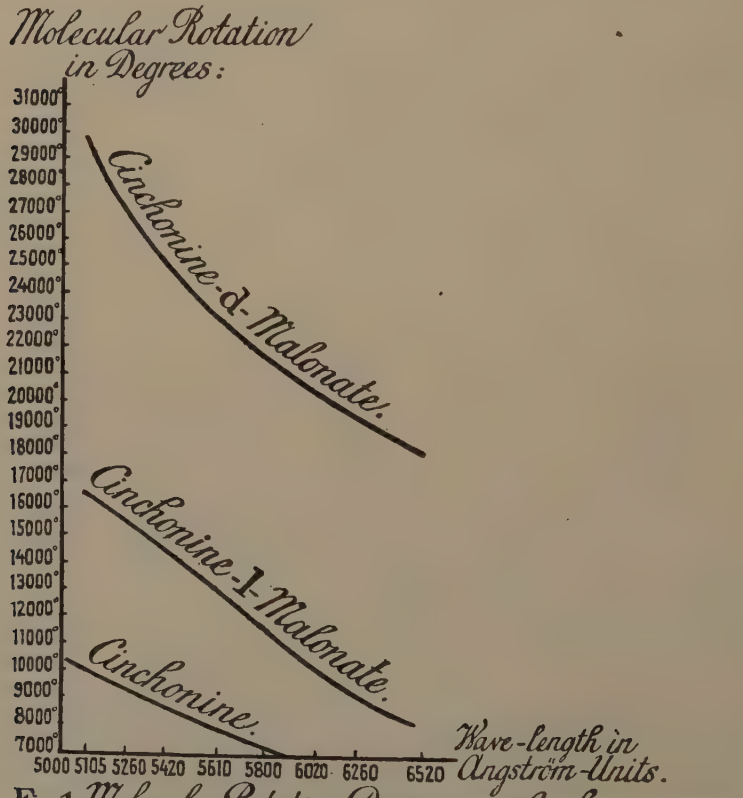

Fig. 1. Molecular Rotation-Dispersion of Cinchonine, and of Cinchonine-d-, and l-Rhodium Malonates.

cinchonine-salt is ground with about ten times its weight of potassium-iodide, and a small amount of water added to the finely pulverized mass. The mixture is allowed to stand for 24 hours at room-temperature; the yellow liquid is then sucked off as sharply as possible from the precipitate. The reddish yellow filtrate is precipitated by 97 °/₀-alcohol, and the pale yellow precipitate of *potassium-rhodium-malonate* thus formed recrystallised from a little water. During the evaporations on the waterbath a noticeable racemisation does not occur. It is advisable to add as little water as possible during the transformation of the *cinchonine*-salt by means of potassium-iodide, as otherwise the precipitation with alcohol is very incomplete.

3. The optically-active components are, like the racemic salt, but in yet higher degree, very soluble; at ordinary temperatures the racemic form is therefore doubtless the stabler phase in comparison with the optically-active components, so that there is no chance to execute a fission by spontaneous crystallisation [1]). The solutions possess a beautiful orange or bloodred colour. For a series of wave-lengths the rotations were determined in the case of both antipodes; the values obtained agreed completely in both cases with exception of the algebraic sign. The concentrations of the solutions used in these experiments must be varied over wide limits, if measurements are to be made over a greater spectral range, because the absorption of the light in layers of 20 cm. is very intensive. In the visible part of the spectrum no distinct absorption-bands occur; but at both ends it is abruptly cut off: a 1,5 °/₀ solution allows the transmission of waves from 5190 to 6800 A. U.; a 0,75 °/₀ solution the transmission of the whole red, yellow, green, and blue part of the spectrum to 4870 A. U.; a 0,37 °/₀ solution in the same way to 4420 A. U.; etc. With a 1,48 °/₀ solution these limits were found at: 5020 and 6900 A. U.

For the polarimetric determinations we used solutions which contained respectively 1,503 grams (*A*), 0,511 grams (*B*), and 0.305 grams (*C*) of the *laevo*gyrate anhydrous salt in 100 grams of liquid; in the case of the *dextro*gyratory antipode we used a solution containing 0,804 °/₀ of the anhydrous salt. The results of these measurements are reviewed in the following table, and in fig. 2 they are plotted in a diagram. The data have been calculated with respect to the anhydrous salt.

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[1]) Conf.: F. M. JAEGER, The Principle of Symmetry and Its Applications to All Natural Sciences, *Amsterdam*, (1917), p. 209, 210.

ROTATION-DISPERSION OF LAEVO- AND DEXTROGYRATORY POTASSIUM-RHODIUM-MALONATE.

Wave-length in *A.U.*	Observed (α) and Molecular (M) rotations of the left salt:						Observed (α) and Molecular (M) Rotations of the right salt:	
	A.		*B.*		*C.*		*D.*	
	α:	M:	α:	M:	α:	M:	α:	M:
4730	—	—	—	—	— 0°,19	2436°	—	—
4870	—	—	—	—	0,19	2436	—	—
5020	—	—	—	—	0,19	2436	—	—
5105	—	—	— 0°,49	— 2524°	—	—	—	—
5180	—	—	0,49	2524	0,20	2564	—	—
5260	—	—	0,50	2575	—	—	—	—
5340	—	—	0,50	2575	0,20	2564	+ 0°,86	+ 2614°
5420	— 1°,50	— 2621°	0,51	2627	—	—	0,87	2645
5515	1,53	2673	0,52	2678	0,21	2692	0,88	2675
5610	1,59	2778	0,54	2781	—	—	0,90	2736
5700	1,61	2812	0,55	2833	0,22	2820	0,92	2797
5800	1,63	2847	0,56	2884	—	—	0,93	2827
5910	1,55	2708	0,53	2730	0,21	2692	0,89	2706
6020	1,47	2568	0,50	2575	—	—	0,85	2584
6140	1,44	2516	0,49	2524	0,20	2564	0,82	2493
6260	1,41	2463	0,48	2472	—	—	0,81	2462
6380	1,38	2410	0,47	2420	0,19	2436	0,74	2402
6520	1,35	2358	0,46	2369	—	—	0,78	2371
6660	—	—	0,45	2317	0,19	2436	—	—
6800	—	—	—	—	0,19	2436	—	—

From fig. 2 the very remarkable shape of the dispersion-curves may be seen, which at a wave-length of about 5800 A. U. show a maximum. For wave-lengths smaller than 5800 A. U. the rotation of the plane of polarisation increases with *increasing* wave-length, while for those greater than 5800 A. U. it diminishes with increasing

wave-lengths, as in ordinary cases. In the neighbourhood of 5800 A. U, the absorption-spectrum, however, does not manifest a single line or band. However the occurrence of such an anomalous rotation-

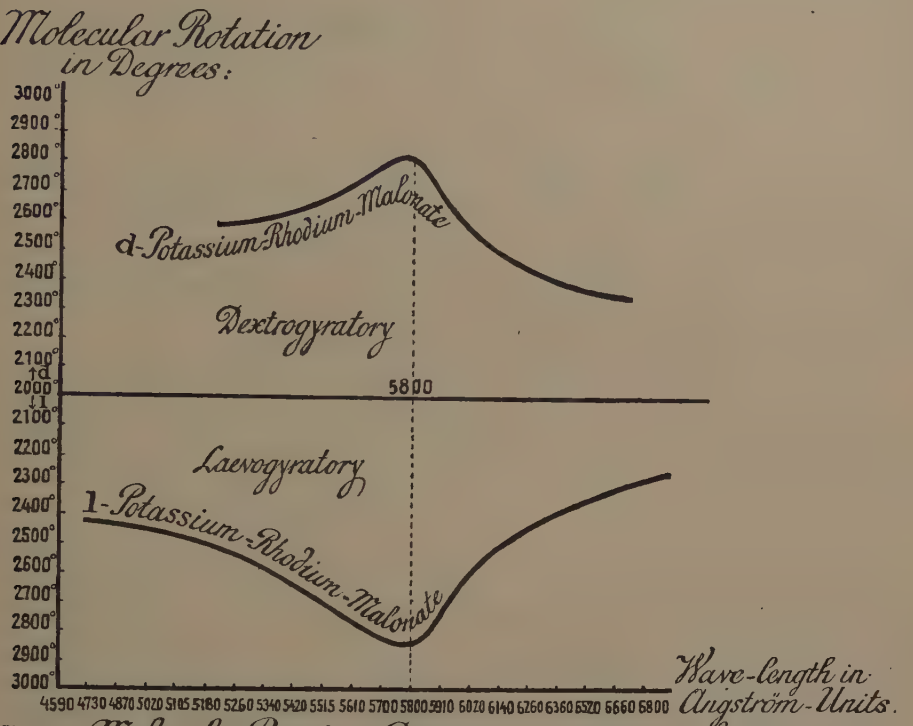

Fig. 2. Molecular Rotation-Dispersion of dextro- and laevogyratory Potassium-Rhodium-Malonate.

dispersion under these circumstances seems to be theoretically explicable, if the assumption may be made that at least two kinds of active ions are present [1]).

Besides this anomalous rotation-dispersion, the whole character of which is in sharp contrast to that of the regular one, the *absolute* activity of these salts appears in general to be appreciably *smaller* than that of the analogously constituted *oxalates*, unregarded the passing through the zero-point in the case of the *oxalate* at 5970 A. U., formerly mentioned. The substitution of the *oxalic acid*-ions:

$$\begin{matrix} COO' \\ | \\ COO' \end{matrix}$$

by the three ions of the *malonic acid*:

$$\begin{matrix} COO' \\ | \\ CH_2 \\ | \\ COO' \end{matrix}$$

around the

[1]) DRUDE, Lehrbuch der Optik, (1900), p. 382.

central *rhodium*-atom, is evidently followed by a very radical change of the character of the optical rotation of the molecule, which affects not only the magnitude, but also the algebraic sign of the molecular rotation for a number of corresponding wave-lengths. The special chemical nature of the substituents placed dissymmetrically round the central atom therefore appears to have as much influence on the magnitude of the rotation, as the chemical nature of the central metal-atom itself.

§ 4. After many attempts we were able to obtain the crystals of the optically-active salts in a measurable form. The laevogyratory component set free from the *cinchonine*-salt of the first fractions, appeared, as already mentioned, to be extremely soluble; the solutions manifested a strong tendency to supersaturation.

By this circumstance the formation of well measurable crystals is severely hindered; and, as generally occurs in such cases, the crystals finally obtained appeared to be badly formed. Because of the vicinal facets present, most crystal-faces yield multiple mirror-images, causing the angular values to oscillate often more than 30′ round their mean-values. Hence it was at first thought, that triclinic crystals were present here. But the repeated determinations, in connection with the optical investigation proved to us finally, that the salt crystallises monoclinically, and more especially in forms differing from their mirror-images.

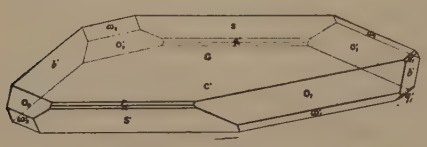

Fig. 3. *Laevogyratory Potassium-Rhodium-Malonate.*

The analogy of the parameters of the optically-active salt and those of the racemic compound is most remarkable, as becomes clear, if the directions of the *a*- and *c*-axes in our former determinations are interchanged [1]).

Monoclinic-sphenoidical

$$a : b : c = 1{,}0637 : 1 : 1{,}1667.$$

$$\beta = 85°27\tfrac{1}{4}'.$$

Forms observed: $c = \{001\}$, predominant, and mostly very lustrous; $b' = \{0\bar{1}0\}$, broad and lustrous; $b = \{010\}$, very narrow, often absent and always yielding good reflexes; $o_1 = \{111\}$, broad and lustrous; $\omega_1 = \{\bar{1}11\}$, narrower than o_1, yielding multiple reflexes; $o_2 = \{\bar{1}11\}$,

[1]) F. M. Jaeger, Proceed. R. Acad. Amsterdam, **20**. 277. (1917). There the ratio $a' : b : c'$ was equal to: 1,0783 : 1 : 1,2309; with $\beta = 86° 36'$.

and $\omega_2 = \{\bar{1}\,\bar{1}\,1\}$, about equally broad, giving sharp reflexes; $s = \{\bar{1}01\}$, broad and well reflecting, but as all faces of the orthodiagonal-zone, often showing oscillating angles; $r = \{101\}$, extremely narrow and dull; $a = \{100\}$, hardly observable, in most cases totally absent; $q = \{021\}$, very narrow and dull. The external habit is that of hemimorphic thin plates parallel to $\{001\}$, with a slight elongation in the direction of the b-axis.

No distinct cleavage could be found.

Angular Values:	*Observed*:	*Calculated*:
$b' : \omega_2 = (0\bar{1}0) : (\bar{1}\,\bar{1}\,1) =$	*50° 46′	—
$c : \omega_2 = (001) : (\bar{1}\,\bar{1}\,1) =$	*60 14	—
$c : o_2 = (001) : (1\,\bar{1}\,1) =$	*55 45	—
$c : a = (001) : (1\,0\,0) =$	85 41	85° 27¼′
$c : s = (001) : (\bar{1}\,0\,1) =$	50 4	50 8
$o_1 : \omega'_1 = (111) : (1\,\bar{1}\,1) =$	64 5	64 1
$s : \omega_2 = (\bar{1}01) : (\bar{1}\,\bar{1}\,1) =$	39 23	39 14
$q : c = (012) : (0\,0\,1) =$	ca. 31 0	30 11
$b' : o'_2 = (0\bar{1}0) : (\bar{1}\,\bar{1}\,\bar{1}) =$	52 49	52 58

On $\{001\}$ the directions of extinction are orientated parallel to and normal to the orthodiagonal. The crystals are not appreciably dichroitic; their birefringence is feeble. The optical axial plane is $\{010\}$, with a feeble, inclined dispersion; one axis emerges on $\{001\}$ at the border of the field.

The crystal-form of the corresponding dextrogyratory antipode is reproduced in fig. 4.

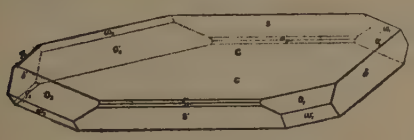

Fig. 4. *Dextrogyratory Potassium-Rhodium-Malonate.*

The specific gravity of the crystals was at 18° C. found to be: $d_{4^0}^{18^0} = 2{,}317$; the molecular volume is therefore: 238,76, and the topical parameters become: $\chi : \psi : \omega = 6{,}1471 : 5{,}7790 : 6{,}7423$. Analysis proved that the salt contains $1\frac{1}{2}$ H_2O; on heating at 120° C. it is decomposed, assuming a brown colour.

If the specific gravity of the racemic compound be also taken into account, ($d_{18^0}^{4^0} = 2{,}251$; $V = 257{,}80$), it appears, in comparing it with the corresponding *potassium-rhodium-oxalate* [1]), that the sub-

[1]) The topical parameters of the *racemic malonate*, after interchange of the a- and c-axis, becomes: $\chi : \psi : \omega = 6{,}2484 : 5.7947 : 7{,}1329$.

stitution of the *malonic acid* for the oxalic acid, causes a diminution of the topical parameters in two, but an enlargement in the third direction as well in the case of the racemic as in that of the optically-active compounds.

At all events this investigation has brought full evidence of the fact, that the salts of the complex *rhodium-trimalonic acid* may also be split into optically-active components, and that the phenomena observed in their study are in agreement with PASTEUR's law in its fullest scope.

Laboratory for Inorganic and Physical Chemistry of the University.

Groningen, June 1918.

Chemistry. — *"Investigations on* PASTEUR'S *Principle concerning the Relation between Molecular and Crystallonomical Dissymmetry:* **VII.** *On optically active Salts of the Tri-ethylenediamine-Chromi-series."* By Prof. F. M. JAEGER and WILLIAM THOMAS.

(Communicated in the meeting of June 29, 1918).

§ **1.** Some time ago it was already found [1]) by one of us, that *racemic tri-ethylenediamine-chromichloride*: $\{Cr(Eine)_3\}Cl_3 + 3H_2O$, was completely isomorphous with the corresponding *cobalti-* and *rhodium-*compounds. We prepared this salt according to a method indicated by PFEIFFER [2]), from the *tripyridyl-chromi-chloride*: $\{Cr(Pyr.)_3\}Cl_3$ by heating this product with ethylenediamine, and subsequent purification. Then it was separated into its optical antipodes by means of *sodium-α-camphor-nitronate* [3]), and these were obtained in this way as the pure *iodides*.

In this fission 6 grams of the racemic salt were dissolved in 20 ccm water, and a solution of 6 grams of pure *sodium-α-camphor-nitronate* in 15 ccm water subsequently added. A pale yellowish precipitate of *d-triethylenediamine-chromi-d-camphornitronate* is formed; it is sucked off and to the mother liquid 2 more grams of *sodium-α-camphornitronate* are then added, and the solution allowed to stand for a few hours, when some more of the precipitate is separated.

After filtration the mother liquid was used for preparing the corresponding laevogyratory component. The precipitate, thoroughly washed with alcohol and ether, was ground in a mortar with an excess of finely pulverised *sodium-iodide*, some water added, and the dark yellow liquid sucked off from the precipitate, which was well washed with alcohol and ether, dissolved in a small quantity of water, and again precipitated by an excess of *sodium-iodide*.

The mother liquid formerly mentioned, containing the *camphor-nitronate* of the *laevo*gyrate salt, was precipitated by addition of 5 grams *sodium-iodide*. The precipitate formed appeared, after being thoroughly washed, to be the *racemic iodide*. The remaining

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[1]) F. M. JAEGER, Proceed. R. Acad., Amsterdam. **20**. 247. (1917).
[2]) P. PFEIFFER, Zeits. f. anorg. Chemie, **24**. 282, 286. (1900).
[3]) A. WERNER, Ber. d. deutsch Chem. Ges. **45**. 865. (1912).

mother liquid, however, was now treated in an analogous way with 8 grams of sodium-iodide; the precipitate appeared to be this time the *laevogyrate triethylenediamine-chromi-iodide*. It is difficult to obtain these iodides in well measurable crystals, and they are moreover ordinarily very small.

§ 2. The rotation-dispersion of these salts was determined in the usual way, already frequently indicated. As the orange coloured liquids already manifested a very appreciable absorption of the transmitted light in layers of 20 c.m. thickness, the measurements for the limiting wave-lengths had to be made with very dilute solutions. These measurements agreed very well with those made in the case of more concentrated solutions, so that for all solutions we have given the mean values of the molecular rotations obtained. In the case of the dextrogyratory component solutions were used, containing 1,0133 grams (*A*), 0,5070 grams (*B*), 0,2535 grams (*C*), and 0,0325 grams (*D*) of the anhydrons salt respectively in 100 grams

Fig. 1. *Molecular Rotation-Dispersion of the Optically active Triethylenediamine-Chromi-Iodides.*

ROTATION-DISPERSION OF THE OPTICALLY-ACTIVE TRI-ETHYLENEDIAMINE-CHROMI-IODIDES.

Wave-length in A. U.:	*Observed Rotation:*		*Molecular Rotation:* (positive and negative)
4260	0.°30	(*D*)	28263°
4320	0 29	*id.*	27321
4420	0.27; 0.35	(*D*, *K*)	25385
4480	0.26; 0.34	*id.*	24552
4570	0.25; 0.33	*id.*	23619
4640	0.23; 0.31	*id.*	22053
4720	0.22; 0.29	*id.*	20858
4790	0.20; 0.28; 0.27	(*D*, *I*, *K*)	18652
4860	0.18; 0.26; 0.24	*id.*	17610
4920	0.16; 0.23; 0.21	*id.*	15128
5020	0.14; 0.40; 0.21	(*D*, *H*, *I*)	13267
5100	0.97; 0.36; 0.18	(*C*, *H*, *I*)	11714
5180	0.88; 0.32; 0.16	*id.*	10579
5260	1.60; 0.79; 1.07	(*B*, *C*, *G*)	9647
5340	1.43; 0.71; 0.95	*id.*	8578
5430	1.27; 0.64; 0.84	*id*	7634
5520	1.12; 0.57; 1.46; 0 72	(*B*, *C*, *F*, *G*)	6692
5610	0.96; 0.48; 1.22; 0.62	*id.*	5741
5700	1.63; 0.81; 0.41; 2.18	(*A*, *B*, *C*, *E*; *F*, *G*)	4891
5800	1.33; 0.67; 0.33; 1.85	*id.*	4093
5910	1.15; 0.56; 0 28; 1.55	*id.*	3422
6020	0.96; 0.47; 0.24; 1.30	*id.*	2912
6140	0.86; 0.43; 0.22; 1.16	*id.*	2621
6260	0.77; 0.38; 0.19; 1.04	*id.*	2328
6380	0.70; 0.35; 0.18; 0.94	*id.*	2133
6520	0.65; 0.32; 0.16; 0.88	*id.*	1951
6660	0.61; 0.30; 0.15; 0.82	*id.*	1820

For these last wave-lengths only the rotations of the solutions *A*, *B*, *C*, and *E* are reviewed.

of the liquid; in the case of the laevogyrate antipode the six different solutions employed contained 1,3512 grams (*E*), *half* or a *quarter* of this (*F*, *G*) in 100 grams of the liquid, and 0,0927 grams (*H*), 0,0464 grams (*I*), and 0,0232 grams (*K*) respectively of the anhydrous salt in 100 grams of the liquid.

The dispersion-curve for the molecular rotation, shewn by measurements is plotted in the diagram (fig. 1). It has much analogy with that of the corresponding *cobalti*-salts, but only a slight analogy with that of the *triethylenediamine-rhodium*-compounds.

Probably the magnitude of the rotation for corresponding wave-lengths in the case of these analogously built complex ions greatly depends on the magnitude of the *atomic volume* of the central metallic atom, in such a way that the rotation appears *higher*, if the atomic volume of the metal is *smaller*. As for instance:

Complex Salt:	Molecular Rotation Observed:	Atomic Volume of the metal:
$\{Co\ (Eïne)_3\}\ I_3 + H_2O.$	$M_{5800} = 7230°$; $M_{5100} = 21580°$; $M_{6600} = 2114°$	6.76
$\{Cr\ (Eïne)_3\}\ I_3 + H_2O.$	$M_{5800} = 4093°$; $M_{5100} = 11714°$; $M_{6600} = 1880°$	7.72
$\{Rho\ (Eïne)_3\}\ I_3 + H_2O.$	$M_{5800} = 3125°$; $M_{5100} = 3965$; $M_{6600} = 2243°$	8.50

The values for $\lambda = 6600$ A. U., are mentioned at the same time for the purpose of demonstrating that this antiparallelism of rotations and atomic volume is surely *not* true for *all* wave-lengths: for rays of *great* wave-length, as e. g. in the visible red part of the spectrum, — the rotation of the *Rho*-salt surpasses even that of both the other salts; only in the domain of appreciable dispersion, is the said regularity met with.

As regards the absorption, we were able to state the following. In a layer of the solution of 20 c.m., a liquid containing.

1,1212% of the salt, allows the passage of all red and yellow rays up to those of 5380 A.U.
0,5606% " " " " " " " " " " " " " " 5220 A.U.
0,2803% " " " " " " " " " " " " " " 5030 A.U.
0,1402% " " " " " " " " " " " " " " 4850 A.U.
0,0701% " " " " " " " " " " " " " " 3940 A.U.

§ 3. Numerous attempts were made to win these *chromi*-salts in well measurable crystals, and to investigate the validity of Pasteur's law also in this case. But a heavy impediment in reaching this aim was created not only by the facility with which those salts decompose in solution, especially under the influence of the light, — but also

by the great solubility of these salts, inducing us always to work with only small volumes of concentrated solutions, from which good crystals are ordinarily deposited with difficulty. For the same reason the transformation of the iodide into the chloride or bromide could not be of any use, so that these for our purpose so very important salts, could not be made use of in this case.

RACEMIC TRIETHYLENEDIAMINE-CHROMI-IODIDE.

$$\{Cr\,(Ene)_3\}\,I_3 + 1H_2O.$$

On slow crystallisation this compound presents itself in the form of very small, orange, apparently octahedral crystals. Crystallisation must occur in the dark, because this salt, in the same way as all the *triaethylenediamine-chromi*-salts, becomes violet under the influence of the light. Also increase of temperature must be avoided, because the solutions change from an orange colour to a dark reddish violet by the transformation into salts of the violet *aquo*-type. The crystals measured were not larger than a pinhead, and often they were disfigured and distorted in rather a strange way. Some of them showed under the microscope the appearance of fig. 2*a*, without

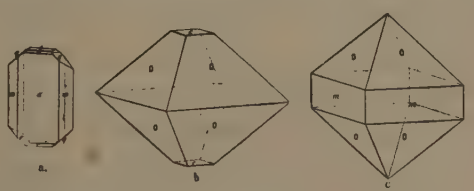

Fig. 2. *Racemic Triethylenediamine-Chromi-Iodide.* $(+H_2O)$.

it being possible however to determine the MILLERian indices of their facets with complete certainty; the crystals pictured in fig. 2*b* and 2*c* manifested however some measurable forms.

Rhombic-bipyramidal.

$$a:b:c = 0{,}8632:1:0{,}8652.$$

The crystals are pseudo-tetragonal, and perfectly isomorphous with the corresponding crystals of the *cobalti*-[1]), and of the *rhodium*-[2]) compound, just as we were able to prove this before in the case of the trigonal *chloride* of this series [3]). The colour of the crystals was orange or red; by partial loss of water of crystallisation, they sometimes get locally yellow and opaque.

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[1]) F. M. JAEGER, Proceed. R. Acad. Amsterdam, **18**. 62. (1915).
[2]) F. M. JAEGER, Proceed. R. Acad. Amsterdam, **20**. 250. (1917).
[3]) F. M. JAEGER, Proceed. R. Acad. Amsterdam, ibid. **247**. (1917).

The forms observed are: $o = \{111\}$, great and very lustrous; $c = \{001\}$, small, but well developed and yielding good reflections; $m = \{110\}$, broad, but commonly with curved and rudimentary facets, and thus practically not well measurable. Probably also a form $q = \{021\}$ occurs, and in the case of the crystals of fig. 2*a* doubtless $a = \{100\}$, as a broad pinacoidal face, and $r = \{h\,o\,k\}$.

Angular values:	*Observed*:	*Calculated*:
$c : o = (001) : (111) =$	*52° 56′	—
$o : o = (111) : (1\bar{1}1) =$	62 49	—
$o : o = (111) : (11\bar{1}) =$	74 10	74° 8′
$o : o = (111) : (\bar{1}11) =$	74 27	74 19

No distinct cleavability was found.

There cannot be the least doubt about the complete isomorphism with the corresponding *Co*- and *Rho*-salt:

Cr-salt . . . . . $a : b : c = 0{,}8632 : 1 : 0{,}8652$.
Co-salt . . . . . $a : b : c = 0{,}8700 : 1 : 0{,}8699$.
Rho-salt . . . . $a : b : c = 0{,}8541 : 1 : 0{,}8632$.

Up till now we have had no opportunity to prove this isomorphism also in the case of the optical antipodes, because no suitable crystals could be obtained. There can be however no doubt, that the said relation also exists in this case.

Laboratory for Physical and Inorganic Chemistry of the University.

Groningen, June 1918.

Anatomy. — "*The Involution of the Placenta in the Mouse after the Death of the Embryo*". By Dr. A. B. DROOGLEEVER FORTUYN. (Communicated by Prof. J. BOEKE).

(Communicated in the meeting of June 29, 1918).

In various species of mammals which are pregnant with several embryos at the same time it accidentally occurs that one or more embryos die before birth. The subsequent fate of the placenta has been controlled in only a few cases and it appears to be intimately connected with the structure of the placenta. Now this structure in the mouse considerably deviates from that in many other mammals. So it seemed to be worth while to investigate in this animal too, as has not yet been done, the involution of the placenta after interruption of the pregnancy. For this purpose the uteri of 8 mice were at my disposal containing together besides many normal egg-chambers 20 egg-chambers without an embryo. Judging from the degree of development of the normal egg-chambers one of the 8 mice had been killed on the 13th day of the pregnancy, one on the 15th, four on the 16th, one on the 17th and one on the 18th day.

The 20 empty egg-chambers are more fully described in a paper that I offered to the "Tijdschrift der Nederlandsche Dierkundige Vereeniging". Here I shall only communicate the results in a general way.

Never was any other trace of the embryo left than some free cells which could not be duly recognised. Many portions of the foetal membranes survived the embryo, but they did not all do so during the same time. So among the empty egg-chambers some groups could be recognised with more or less remainders of the foetal membranes.

In the first group the giant-cells (in the mouse trophoblastic cells which are greatly enlarged and have become independent) and the membrane of REICHERT were left and moreover parts of the ecto-placental cone and of the proximal or distal entoderm of the yolk-sac or of both. The proximal entoderm of the yolk-sac could be well recognised by the appearance of the cells, but it had always been broken into pieces. The distal entoderm of the yolk-sac sometimes lined large pieces of the membrane of REICHERT internally; besides free cells of it occurred. The ectoplacental cone

never inclosed embryonic blood-vessels, but sometimes some connective tissue of the allantois entering the ectoplacental cone together with the large blood-vessels. Always the cells or the syncytium of the ectoplacental cone could be recognised. In some cases they changed into young giant-cells, which in normal circumstances too can originate from cells of the ectoplacental cone. Often spaces filled with maternal blood lay between the cells of the ectoplacental cone, as is the case in normal egg-chambers. REICHERT's membrane could easily be recognised as the homogeneous membrane that develops beneath the trophoblastic epithelium when it changes into free giant-cells. After the disappearance of the embryo the contraction of the uterine wall had pressed the greater part of the ectoplacental cone into the space previously occupied by the embryo. Moreover this contraction had folded REICHERT's membrane. Sometimes this membrane had much diminished in size, but it always showed the aperture through which the cells of the ectoplacental cone previously cohered with the allantois.

Generally the giant-cells very clearly showed their power to ingest erythrocytes and other portions of the maternal decidual tissue, but they had hardly changed in this group. This was not so in the second group of empty egg-chambers where, as to the foetal elements, only the distal entoderm of the yolk-sac, the membrane of REICHERT and the giant-cells were left. There several of the latter cells had grown out till they reached dimensions that were extraordinary even for giant-cells. In normal egg-chambers it is the task of the giant-cells to attack the decidual tissue and the maternal blood and to leave part of the ingested food to the embryo. As soon as they have been loosened from the trophoblastic epithelium or the ectoplacental cone they lead an independent life. After the death of the embryo the only change is the fact that of course the giant-cells can provide no longer any food to the embryo. They keep all to themselves and consequently thrive extraordinarily. In all directions they acquire the same dimensions, as the pressure of the embryo which in normal egg-chambers flattens them much, has been suspended. Therefore the space occupied by the giant-cells is much larger than in normal egg-chambers. Their number only seems to me to be larger, because they are not dying away so soon as in normal egg-chambers, not because more of them would have developed. Yet here too the fate of the giant-cells is to die away. This is more conspicuous in another group of empty egg-chambers where giant-cells are the only foetal element that is left. Especially here one sees the body of the giant-cell losing its affinity for the dyes

and dissolving, leaving the naked nucleus behind. Afterwards the nucleus submits to the same fate.

The giant-cells have not been able to consume the whole layer of decidual tissue before they disappear. Yet this layer must be removed if the normal situation of the uterine-wall is to return. Therefore the giant-cells are supported by another type of cells, apparently amoeboid wandering cells with phagocytal qualities. These cells are of a hitherto unknown kind and in normal egg-chambers they do not occur, not even post partum. Their shapes and sizes are very variable. They have a nucleus which generally lies excentrically and sometimes two or more nuclei. Their cytoplasm stains remarkably intenseley with eosin dissoluble in water, whereas eosin dissoluble in alcohol stains them, it is true, but not extraordinarily. I propose to call these cells eosinophilous phagocytes. About their origin nothing is known to me, but I think that they are maternal cells. The eosinophilous phagocytes were lacking only in one of the twenty empty egg-chambers, and this one obviously had been preserved within a day after the death of the embryo. In the first place they appear in small groups between the group of giant-cells and the layer of unattacked decidual tissue. These groups enlarge into constantly thicker layers, which are always situated either between the decidual tissue and the giant-cells or between the former and the uterine cavity. The eosinophilous phagocytes attack only the maternal decidual tissue and not the giant-cells and they continue to do so after the disappearance of the giant-cells. So a fourth group of empty egg-chambers exists where one sees no foetal rests at all, but only eosinophilous phagocytes which remove the layer of decidual tissue, which has in the mean time greatly diminished in size. I could not observe the disappearance of the eosinophilous phagocytes.

As is known, in egg-chambers of the mouse the uterine cavity disappears at the mesometrical side of the embryo to extend at the antimesometrical side of the embryo starting therewith from the portions of the uterine cavity that are lying between the egg-chambers. Before the parts of the new uterine cavity reach one another in the middle of the egg-chamber, which occurs on the 17th day of the pregnancy, a more or less thick partition of decidual tissue in the egg-chamber separates the parts of the new uterine cavity, which approach one another. Now this partition can be found in many empty egg-chambers, but in some it has been ruptured, in others it is attacked by eosinophilous phagocytes, and in still others it has been removed prematurely by eosinophilous phagocytes.

I cannot even guess the cause of the death of the embryo, but I observed that the embryo may perish at different ages. At least I think I have met with a case where this occurred on the 8th day and with another where this occurred on the 16th day. He who disposes of younger specimina (my youngest embryos were of the end of the 13th day) probably will also find eggs that have perished before the 8th day. Moreover it appears that in one and the same uterus embryos may die away at very different ages. I discovered in the same uterus one of the empty egg-chambers with the smallest and one with the greatest quantity of foetal rests, and I conclude that one embryo had been dead a much longer time than the other.

Leiden. *Anatomisch Kabinet.*

Physics. — "*The Limit of Sensitiveness in the String galvanometer.*" By Prof. I. K. A. WERTHEIM SALOMONSON.

(Communicated in the meeting of June 29, 1918).

In EINTHOVEN's stringgalvanometer the deflectional constant is subjected to the same law as holds good in the movable needle- and movable coil galvanometer: it is proportional to the square of the periodic time of the movable part. In the string instruments the duration of the oscillations is modified by altering the tension of the string. The sensitiveness finally depends on this tension as well as on the dimension and material of the string, and lastly on the strength of the magnetic field.

The tension of the string can only be altered within certain limits. The upper limit is given by a tensile stress exceeding the elastic strength. The lower limit is the total absence of tension. But even when no pull is exerted, the string can still vibrate transversally. The frequency of the vibrations it then makes, is a function of the dimensions of the wire and two properties of the material i.e. density and the elasticity-modulus, and may be represented by

$$N = \frac{m^2}{8\pi}\frac{d}{l^2}\sqrt{\frac{E}{g}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which N denotes the frequency, l the length, d the diameter of the string, g being the density and E YOUNG's modulus, whereas m is the smallest root of the transcendental equation $\cos m \cos h\, m = 1$. The value $m = 4.730\ldots$ (RAYLEIGH On sound I. Art. 174).

As we may discard the influence of temperature on the elasticity, this formula gives the lowest frequency for transverse vibrations obtainable in strings, which in a definite material and with given dimensions cannot be lessened. We may therefore say that the periodic time of the string in the EINTHOVEN galvanometer, and consequently the sensitiveness of the latter is limited by the impossibility to lessen the frequency; and as the elasticity of the material is responsible for transverse vibrations which might occur in a perfectly relaxed wire, the true limit of the sensitiveness is to be found in the elasticity, and as we shall see also in the density and specific resistance of the material of the strings.

With the formula (1) we can always calculate the minimum of

the frequency of the transverse vibrations of the string, if we know its dimensions and the material of which it is made. In table I a few numerical data are given regarding various materials which may be used for making strings. In this table the length is taken as 10 cm and the diameter as one micron (10^{-4} centimeter).

TABLE I.

	$E\frac{1}{98100000}$	g	N/sec.	T
Cu	11000	8.9	0.3100	3.32″
Ag	7500	10.5	.2356	4.25
Au	7500	19.2	.1724	5.80
Al	6750	2.7	.4408	2.27
Pt	16500	21.4	.2448	4.08

It is very difficult to measure directly the vibrations per second in wires of 1 micron diameter. The air resistance in this case is so considerable as to cause the movement to come to a dead stop. We should have to examine such strings in a perfect vacuum. Furthermore we are not able to make wires of 1 micron except in platinum, and perhaps in aluminium and gold. Silver wires of 1 micron are as yet not attainable. But the dimensions used in this table and the figures in the last columns permit us to calculate in a simple way, e.g. with a slide rule, any periodic time when other dimensions are given: the vibration time being proportional to the square of the length and inversely proportional to the diameter.

A wire clamped at the end without any tensile stress will sag under the influence of a load P, uniformly distributed over the total length. The maximum deflection h will be

$$h = \frac{P}{EI}\frac{l^3}{384} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where I represents the axial moment of inertia of a section of the wire. As for a round wire $I = \frac{\pi d^4}{64}$, we get

$$h = \frac{Pl^3}{6\pi E d^4} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In the string galvanometer the transverse load P is equal to Hil Dynes, if H be the strength of the magnetic field in Gausses, i

the current strength in Webers (= 10 ampere) and l the length of the wire in centimeters. If we put this value for P in 3):

$$h = \frac{H i l^4}{6\pi E d^4} \quad \ldots\ldots\ldots \quad (4)$$

giving the deflection of the middle of a string clamped at the ends without tension, and of a length l and a diameter d, placed in a magnetic field H, as soon as a current of i Weber passes through the string. We need hardly insist on the fact that this formula gives the absolute limit for the sensibility for small currents.

The next table II shows this limit for strings made of different materials. For the dimensions of the string we again take 10 cm and 1 micron, for the current-strength 10^{-13} Weber (10^{-12} ampere), for the field intensity 10000 Gauss. The last column gives the deflection in millimeters if the absolute deflection of the middle be magnified 1000 times. We can use the figures of this column, if we wish to calculate the possible deflection with strings of other dimensions in a field of a different strength, and when observed magnified to another scale. The deflections are proportional to the fourth power of the length and the inverse of the diameter of the string.

TABLE II.

	$E\frac{1}{98100000}$	$\frac{Hi}{6\pi E}$	Deflection $\left\{\begin{array}{l} V = 1000\times, d = 1\mu \\ l = 10\,\text{cm}, i = 10^{-13}\ \text{WEBER} \end{array}\right.$
Cu	11000	4916.10–20	49.16 mm
Ag	7500	7210.10–20	72.10 „
Au	7500	7210.10–20	72.10 „
Al	6750	8012.10–20	80.12 „
Pt	16500	3277.10–20	32.77 „

The figures in the last column may also serve to calculate figures for existing strings. With an aluminium string of 2 microns and 56 millimeters' length in a field of about 16000 Gauss, I found a deflection of 0.40 millimeters for 10^{-12} ampere, which took place in about 20 seconds. From the figure in the table we calculate that the deflection ought to be 1.20 millimetres. In EINTHOVEN's publications on silvered quartz fibres we equally find figures about the possible sensibility, the order of which does not disagree greatly with the theoretically possible deflection if we take for the sensitiveness with silvered quartz fibres the same value as in the case of silver

wires. The same may be said about my own observations with quartz fibres. Generally the deflection actually observed is some 3—5 times smaller than we ought to expect from the theory. The explanation is found when we consider the behaviour of silver strings of 16.5 microns and of copper strings of 15 microns diameter. These wires still give vibrations when the tension is reduced as far as possible, but in every case the frequency is about 1.5 to 2.1 times greater than that calculated from formula (1). With a silver string of 16.5 μ and 53 mm length I could not reduce the frequency under 20 per second instead of 14 as calculated. When magnified 47 times 1 microampère caused a deflection of 1.31 millimeter; the string being placed in a field of 14000 Gauss. The theoretical value is 3.7 millimetres with 14 vibrations, which would come to about 1.8 millimeters with 20 vibrations. As there may be a slight difference between the figure taken for the diameter and the actual diameter, the agreement may be considered not unsatisfactory, the more so as the value of E must also be considered as merely an approximate one. Finally we must state that the string was not an entirely straight one, and that in being mounted it had probably retained a slight torsional stress.

In a few other observations of the same kind with wires of different material I found a deflection of 8.1 mm where 9.1 mm was expected; also one of 36 mm, where 40 had been calculated. Generally speaking, the agreement was by far the best with the thicker wires. Yet in all cases the agreement was close enough to allow an extension of the theory to the sensitiveness for small potential differences.

From the formula (4) we find an expression for the sensibility for small potential differences by dividing both parts by w, the resistance of the string:

$$\frac{h}{w} = \frac{Hl^4}{6\pi E d^4 w} \quad \ldots\ldots\ldots \quad (5)$$

This formula gives the deflection in centimeters of the middle part of the string when a potential difference of 10 Volts is applied to the terminals. But with this formula we have not taken count of the damping. The movement of the string in the EINTHOVEN galvanometer is damped partly by air friction, partly by electromagnetically generated counter-electromotive force. In the following cases we shall consider only the electromagnetic damping, which with thick wires greatly exceeds the air resistance. As the electromagnetic damping is caused by the number of the lines of force

cut by the string during its movement, the form taken by the string in its deflected condition is of the greatest significance as well as the strength of the magnetic field. A string under tension deflected in a homogeneous magnetic field takes the form of a parabola. In that case the damping factor is

$$D = \tfrac{2}{3}\,\frac{H^2 l^2}{w \cdot 10^9} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Whenever the string would take another form whilst being deflected, the factor $\frac{2}{3}$ would take another value. This factor represents the mean deflection taken over the whole string as compared with the maximum deflection. A perfectly relaxed string, clamped at the ends and uniformly loaded takes the form given by the formula

$$y = \frac{P}{EI}\,\frac{l^3}{24}\left(\frac{x^2}{l^2} - 2\,\frac{x^3}{l^3} + \frac{x^4}{l^4}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

in which y gives the deflection for a point at distance x from the end. If we put $x = \frac{1}{2}l$ we get the deflection for the middle of the string, which has already been given in formula (2). In order to find the mean deflection we integrate (7) over the whole length:

$$y \int_0^l dx = \frac{P}{EI}\,\frac{l^4}{720} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Comparing (2) and (8) we find

$$y \int_0^l dx / y_{max} = \frac{8}{15}$$

so that we may state

$$D = \frac{8}{15}\,\frac{H^2 l^2}{w \cdot 10^9} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Taking M as the mass of the string, we can always represent the time of vibration as

$$\frac{1}{N} = 2\pi \sqrt{\frac{M}{K}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

if K be a lateral force and if we suppose the damping to be very slight. If the string should make critically damped vibrations, the damping would be

$$D = \sqrt{4\,MK} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Eliminating K from (10) and (11) we get, in connection with (9)

$$4\pi\,MN = \frac{8}{15}\,\frac{H^2 l^2}{w \cdot 10^9} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

In (12) we substitute for the mass $M = \pi d^2 lg$ and for the resistance $w = \frac{l\varrho}{\pi d^2}$, giving:

$$H^2 = 7.5\,\pi\,10^9 \,.\, g\,\varrho\,N \,. \,. \,. \,. \,. \,. \,. \quad (13)$$

which shows a simple relation between the allowable and necessary strength of the magnetic field, the frequency and the density and resistivity of the material. If we were at liberty to choose any figure for N, the length and the thickness of the string would seem to be of no consequence. But we started from the premise that the frequency should be as small as possible with a string of predetermined length and thickness, and elasticity. Hence we must put the value for N taken from (1) in (13) giving

$$H = 1.45\,10^5 \sqrt{\frac{d}{l^2}} \sqrt[4]{g\,E\,\varrho^2} \,. \,. \,. \,. \,. \quad (14)$$

Now we can substitute this value for H in (5) and by likewise substituting $w = \frac{\varrho l}{\pi d^2}$ we arrive at a formula for the sensibility for potential differences:

$$\frac{h}{\iota w} = 6040 \frac{l^2}{d\sqrt{d}} \cdot \sqrt[4]{\frac{g}{E^2\varrho^2}} \,. \,. \,. \,. \,. \quad (15)$$

This expression for $h/\iota w$ gives the extreme limit for the sensibility of a completely relaxed string in a magnetic field of a strength exactly calculated to render the movements of the short-circuited string critically damped. The volt-sensibility increases by l^2 and decreases by $d\sqrt{d}$. It also depends on the density, resistivity, and elasticity of the material. In table III we find the constants for different materials and in the fourth column the comparative "material-factor" for each material. These have been multiplied by 10^5 so as to indicate deflections per microvolt with strings of 1 μ

TABLE III.

	g	$E.\frac{1}{98100000}$	$\varrho.10^6$	$6040.\sqrt[4]{\frac{g}{E^2\varrho^2}}.10^5$	H	N/sec
Cu	8.9	11000	1.62	774	325	0.3100
Ag	10.5	7500	1.75	1034	320	0.2356
Au	19.2	7500	2.20	1073	417	0.1724
Al	2.7	6750	2.87	622	284	0.4408
Pt	21.4	16500	9.40	295	1078	0.2448

diameter and 10 c.m. length with a microscopic magnification of 1000 times. The next column shows the strength of the field H in Gauss, and the last column contains once more the frequencies.

Gold fibres, if critically damped, will give a larger deflection than strings of any other material, but of the same dimensions. The time of vibration, and consequently the time of deflection is larger than with other strings. Hence we cannot easily compare the results. This table is only useful if we wish to calculate the possible deflection with strings of other dimensions. In order to get comparable figures we shall have to consider strings of the same diameter, which have the same vibration time. A formula for this case can be given by calculating

$$\frac{h}{iw} \cdot N = 5400 \frac{1}{\sqrt{d}} \cdot \frac{1}{\sqrt[4]{E\varrho^2 g}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

This formula represents the deflection caused by 10 Volts through a string of a diameter d, completely relaxed, and vibrating once a second, whilst placed in a magnetic field of a strength, sufficient to cause the movement of the string to be entirely damped. In this case the length is predetermined for any material by the condition that the frequency is one per second.

In table IV we give a few figures which can be calculated by this last formula.

TABLE IV.

	$\frac{5400}{\sqrt[4]{E\varrho^2 g}}$	H	l	w	Deflection per μV. with $d = 1\mu$. and $V = 1000$ ×
Cu	2410	590	5.56	1150	241 mm
Ag	2448	658	4.85	1080	245 „
Au	1878	997	4.15	1163	188 „
Al	2757	426	6.63	2430	276 „
Pt	726	2190	4.95	5940	73 „

From this table we see that aluminium is the best material for strings in an EINTHOVEN galvanometer if used for the measuring of small potential differences. A string of 1 μ, completely relaxed and 6.65 cm in length, gives vibrations of one second. With it we can get a deflection of 276 mm for 1 microvolt, if the field be adjusted at 997 Gausses; and the microscopic magnification amounts

to 1000 times. If the string were placed in a perfect vacuum the movement would be critically damped. Silver follows with 245 mm deflection if the length be 4.85 cm. Copper requires a longer string viz. of 5.56 cm and gives about the same deflection. Practically we shall have to make our choice between aluminium, silver, or copper, whenever we want a high sensitiveness for small potential differences with a critically damped movement. From the formula we conclude that with a given material the thinner the string the higher will be the sensibility for small potential differences.

Finally we shall have to consider one other possibility for rendering the voltsensibility as high as possible.

We take again the case of a perfectly relaxed string, clamped at the ends. If the weight P be uniformly distributed over the entire length l, we must use the formula (1). But if the string is loaded in the middle only with the weight P, the deflection will be exactly twice as large:

$$h = \frac{P}{EI}\frac{l^3}{192}. \quad \ldots\ldots\ldots \quad (17)$$

If we put the string, of a length l in a stronger magnetic field H' but of a very short length λ so as to make $Hl = H'\lambda$, and if we suppose λ to be very small as compared with l, we shall come very near the conditions represented by the last formula (17). Especially if we use strings of not too small a diameter there will be scarcely any difficulty of making the magnetic field 10— 20 times stronger and the string 10—20 times longer than the field. In this case we practically double the deflection, but at the same time the damping will have become too great. The damping factor will have become nearly 1.0 instead of 8/15. Hence the magnetic field must be made $\sqrt{2}$ times weaker. Finally the sensibility for small potential differences will become only $\sqrt{2}$ times greater.

Anatomy. — *"The egg-cleavage of Volvox globator and its relation to the movement of the adult form and to the cleavage types of Metazoa."* By Dr. H. C. DELSMAN. (Communicated by Prof. J. BOEKE).

(Communicated in the meeting of June 29, 1918).

For the zoologist still more than for the botanist *Volvox* is an interesting object. Already in this organism, where it is still dubious whether we have to consider it as a plant or as an animal, we see indicated the main lines along which the phylogenetic development of the Metazoa has taken its course. BÜTSCHLI [1]) rightly observes that *Volvox* is no longer to be considered as a colony of Protozoa, but as a pluricellular organism of simple structure. Not only do the cells communicate with each other by plasmodesms, forming thus one single mass of protoplasm, but also there is a difference between mortal somatic and potentially immortal propagation cells as is characteristic of Metaphyta and Metazoa. Between these two *Volvox* holds an intermediate position, reminding one more of the former by the possession of chlorophyll but pointing more in the direction of the animal kingdom by the rest of its organisation.

Long ago the first stage of development in Metazoa, the blastula, has been compared to *Volvox* and was termed by HUXLEY [2]) e.g. "the animal Volvox". The resemblance afterwards appeared to be still greater than HUXLEY could have suspected, for *Volvox* is by no means a homaxone sphere rotating indiscriminately in all directions, but shows a distinct opposition between an animal and a vegetative pole. The line joining them can be described as the main axis of the organism, which is not strictly globular, but a little elongated in the direction of the main axis. With the animal pole directed forwards it swims with a rotary movement round the main axis just as is the case with the pelagic larvae of lower Metazoa and also still of *Amphioxus*. At the animal pole the cells are smaller and further from each other and contain also less chlorophyll than those at the vegetative pole which are darker green, by reason of the higher

1) O BÜTSCHLI, 1883—1887, Protozoa II, p. 775, in BRONN's Klassen und Ordnungen des Thierreichs.

2) T. H. HUXLEY, 1877. The Anatomy of Invertebrated Animals, p. 123, 678.

proportion of chlorophyll, and communicate by more numerous and broader plasmodesms. The cells at the animal pole each contain a red stigma as characteristic of flagellates sensible to light (to which also the Volvocinea belong), whilst those at the vegetative pole are lacking them. The two kinds of cells pass quite gradually into each other. The propagation cells are restricted to the vegetative half. Any one having an opportunity to study *Volvox* can easily verify all this.

The propagation occurs either by means of egg-cells and spermatozoa, or parthenogenetically by so-called parthenogonidia. The latter mode occurs, just as in Rotatoria and Infusoria, during a number of generations, the former mode at the close of such a period, the encysted egg being the result. The cleavage stages of the egg and of the parthenogonidia in which development proceeds in a similar manner, exhibit again a striking resemblance to those of Metazoan eggs. The figures given of these stages for *Volvox*, *Pleodorina*, *Eudorina*, *Pandorina*, and *Gonium*, remind one especially of stages of the spiral cleavage type, which probably we may designate as the original cleavage type of the Zygoneura or Protostomia, and which is still found with Polyclads, Nemertines, Polychaetous Annelids and most Molluscs. It therefore seemed to me very interesting to find out how far the cleavage of *Volvox* corresponds to the spiral type. The statements made by former investigators appear to be insufficient and too contradictory to answer this question in a satisfactory way [1]).

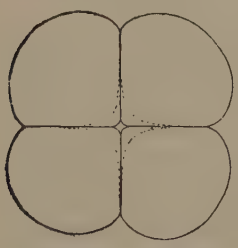

Fig. 1. *Volvox globator*, parthenogonidium, four-celled stage, seen from the vegetative side.

When, therefore, the opportunity presented itself to study more closely the cleavage of the parthenogonidia in *Volvox*, which appeared

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[1]) Statements on the cleavage of *Volvox* are found in:

J. Goroshankin, 1875, Genesis im Typus der palmellenartigen Algen. Versuch einer vergleichenden Morphologie der Volvocineae. Mitt. Kaiserl. Ges. naturf. Freunde in Moskau, Bd. 16 (Russian, an extract is found in Botan. Jahresber. f. 1875, p. 27).

E. Overton, 1889, Beitrag zur Kenntniss der Gattung Volvox. Botan. Centralbl., Bd. 10, p. 177.

L. Klein, 1890, Vergleichende Untersuchungen über Morphologie und Biologie der Fortpflanzung bei der Gattung Volvox. Ber. naturf. Ges. Freiburg, Bd. 5, p. 15.

to occur in considerable number in the *Victoria regia*-basin of the Leyden botanical garden, I readily seized it. The study was made on living material. During development the parthenogonidium, which continues to communicate by plasmodesms with the surrounding cells, considerably increases in size [1]), so that the older stages are often easier to study than younger ones, for which the use of oil-immersion as a rule is to be preferred.

By two meridional cleavages the parthenogonidium is first divided into four equal cells, which each will give rise to a quadrant. The eight-celled stage has already been figured repeatedly for *Volvox* and other Volvocinea, but not the transition of the four- into the

Fig. 2. Beginning of the third cleavage, animal side

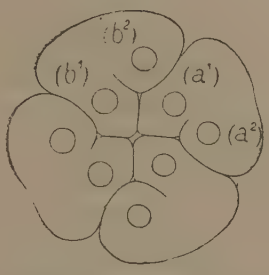

Fig. 3. Transition 4—8, vegetative side

eight-celled stage. Figs. 1, 2, and 3 teach us that during this cleavage a torsion amounting to 45° occurs between what we may call for the sake of shortness the four vegetative cells and the four animal cells. In the terminology of the spiral cleavage type we should call this torsion a dexiotropic one since, if we look at the egg from the side of the animal pole, the four animal cells appear to lie to the right of the four lower cells.

It seemed to me interesting to make out if this third cleavage always takes place in the same way or if, as could equally be imagined, it is sometimes dexiotropic and sometimes laeotropic. In the cleavage of *Balanus*, which shows a similar torsion, I found e.g. both possibilities occurring indiscriminately [2]). In the spiralcleavage type the third cleavage is always dexiotropic with the exception of inversely wound Gasteropoda where the whole cleavage proceeds in an inverse manner. So not only the adult form but equally the earliest cleavage stages present the reflected image of what we find in dextral Gasteropods.

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[1]) All the figures in this article have been drawn the same size.

[2]) H. C. Delsman, 1917. Die Embryonalentwicklung von Balanus balanoides Linn. Tijdschr. Nederl. Dierk. Ver. (2), Dl. 15.

I found that in *Volvox* the third cleavage always proceeds in a dexiotropic manner, and the suggestion lies at hand that here too some peculiarity of the adult form might stand in a certain relation to this phenomenon. What, for example, is the direction in which *Volvox* rotates round the main axis, is this always the same or at one time dexiotropic and at another laeotropic? As has been already observed by earlier investigators and as I can confirm here once more, the rotation always occurs in this way that, seeing it from the animal pole, we may designate it as clockwise, i.e. in the direction of the hands of a clock or dexiotropic. It lies at hand to suggest a relation between these phenomena, as has been stated equally in Gasteropods. That in the latter there can be no question of a direct causal relation between the torsion of the adult animal and that of the cleavage cells will be evident at once if we bear in mind that the spiral cleavage type occurs equally well in forms that are not wound at all, as Lamellibranchiata, Chitons, Polychaetous Annelids etc. We will revert to the question whether possibly in *Volvox* we might think of a more direct relation between the torsion during cleavage and the direction of the rotation during movement.

In the eight-celled stage (fig. 4, 5) which has been figured already

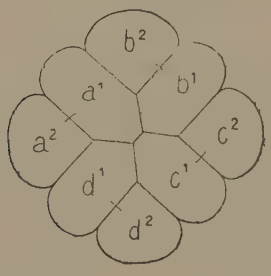

Fig 4. Stage 8, animal side.

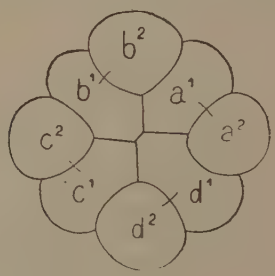

Fig. 5. Stage 8, vegetative side.

more than once, the four vegetative cells alternate with the four animal cells. They constitute together a little cell-plate representing phylogenetically the *Gonium*-stage, but which at the border already begins to curve in. This curving in accentuates itself during the transition into the 16-celled stage and in *Volvox* evidently manifests itself somewhat earlier than in *Pleodorina*, *Eudorina*, and *Pandorina*, where also in the stage 16 the cells are still lying in a concave little plate, while in *Volvox* it has then already passed into a hollow globule with an opening, the "phialoporus". The eggs always have the vegetative side, with the phialopore, directed to the surface of the maternal organism.

The passage of the eight- into the sixteen-celled stage, which in the spiral type is always performed by a laeotropic cleavage, is characterised in *Volvox* by a progressive torsion of the cells of the vegetative side with regard to those of the animal side and this in

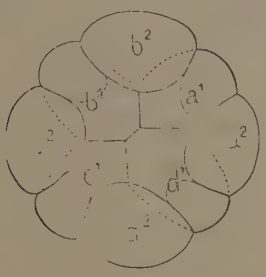

Fig. 6. Beginning of the fourth cleavage, vegetative side.

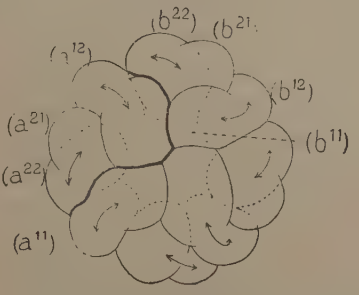

Fig. 7. Transition 8—16, animal side.

the same direction in which it has already manifested itself in the foregoing cleavage, which is what we may call dexiotropic. This expresses itself in the shape of the cells immediately when the fourth cleavage sets in, as fig. 6 teaches us. The torsion here has already become a little greater than 45° as becomes evident if we compare the situation of the inferior parts of the vegetative cells (a_2—d_2) with regard to the cross of the cleavage furrows at the animal pole.

The fourth cleavage (fig. 7, 8), therefore, under the influence of

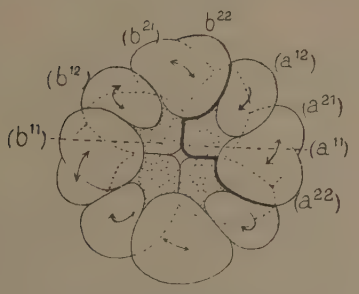

Fig. 8. Transition 8—16, vegetative side.

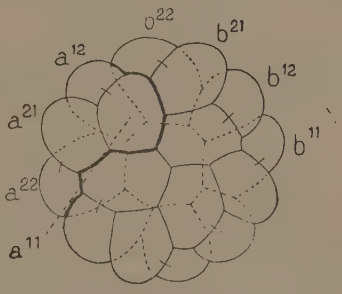

Fig. 9. Stage 16, animal side.

the above torsion, must be described as dexiotropic. For this reason, and in regard to the further cleavage, I think it inadvisable to apply here the nomenclature proposed by CONKLIN for the spiral type, but will modify this a little. I call the cells of the four quadrants resp. *a*, *b*, *c*, and *d*, and to their descendants I give each time the exponent 1 to the cell that lies to the animal side, and the exponent 2 to that lying to the vegetative side. Thus all the cells with the letter *a* are descendants of the cell *a* of the four-celled stage, forming

together one quadrant which, moreover, I have surrounded with a thick line in the figures. Now fig. 9 answers wholly to the image presented by a 16-celled stage of the spiral cleavage type, however, one would expect the cells a^{11}, a^{12}, b^{21} and b^{22} to represent together one quadrant. This has been shown not to be the case, and if one takes a view of figs. 8 and 9, the dexiotropic torsion that has occurred during the cleavage, at once strikes the eye. Between a^{11} and a^{22} this torsion now amounts to between 45° and 90°. The phialopore is surrounded by the cells a^{22}—d^{22} and a^{12}—d^{12}, the former constituting the four longer, the latter the four shorter sides of the octangular phialoporic border. Sometimes one of the cells a^{21}—d^{21} also reaches the border, the latter then being formed by nine cells.

The fifth cleavage, leading to the 32-celled stage, is again laeotropic, as is shown as well by a view from the animal (fig. 10) as from the vegetative side (fig. 11). Thus the dexiotropic torsion is again

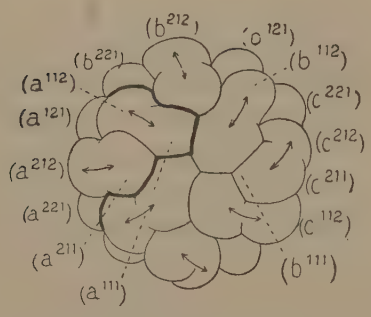

Fig. 10. Transition 16—32, animal side.

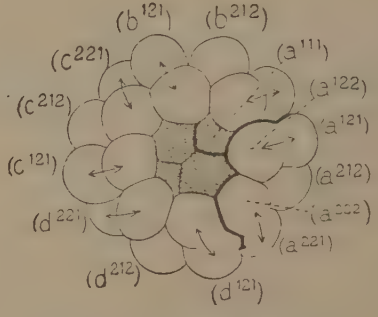

Fig. 11. Transition 16—32, vegetative side.

continued here, and as fig. 11 and especially fig. 13 shows, this torsion of the vegetative extremity of each quadrant with regard to the animal extremity (the cell a^{111}) now amounts to nearly 90°. While the cell a^{212} forces itself between a^{12} and a^{22}, as was already the case in the 16-celled stage, so that a^{221} is pushed aside a little (figs. 11, 13), a^{12} while dividing is pushed to the phialoporic border by a^{11}, which also divides. As a consequence a^{122}—d^{122} now form the longer, a^{222}—d^{222} the shorter sides of the octangular phialopore. Often also all eight sides are of equal length.

The arrangement of the cells in the 32-celled stage is so regular (figs. 12 and 13) that no doubt one would not suspect from it the torsion stated here by watching the cleavages.

The last cleavage studied by me is the one that leads from the 32-celled to the 64-celled stage (figs. 14 and 15). The direction of

the divisions gradually becomes subject to more variation, yet the equatorial direction just as in former cleavages — though with a

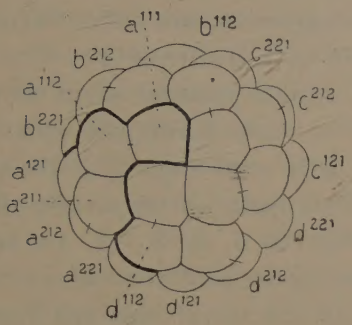

Fig. 12. Stage 32, animal side.

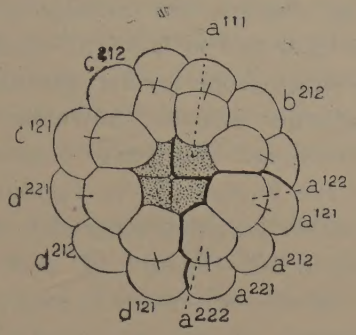

Fig. 13. Stage 32 (the same egg), vegetative side.

deviation caused by the torsion — continues to predominate. That the torsion still proceeds is evident from fig. 15, which shows that it is already more than 90°.

At the beginning of this investigation I almost expected to find that *Volvox* divides according to the spiral cleavage type. The figures given by some investigators seemed to me to point in this direction. No doubt this result would have been interesting with regard to the derivation of the different cleavage types of Metazoa and their mutual relation. A more direct relation between *Volvox* and the lowest forms with a spiral cleavage type would not then appear improbable, since, as shown above, there are other points of agreement. That *Volvox* possesses chlorophyll would be no insuperable obstacle

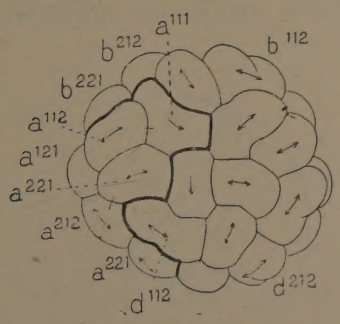

Fig. 14. Transition 32—64, animal side.

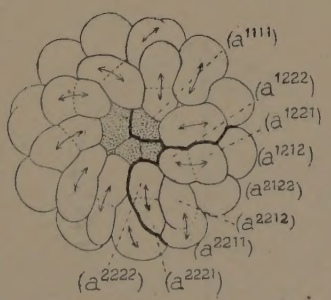

Fig. 15. Transition 32—64, vegetative side.

since it can hardly be doubted that animals must descend from organisms with chlorophyll. No production of organic from inorganic substance would have been possible otherwise.

We have seen, however, that the cleavage of *Volvox* may not be counted as belonging to the spiral type in the form in which it occurs in Metazoa, though the arrangement of the cells is more in a spiral than it is with the latter. Though there are certain points in common I yet refrain from further speculations in this direction.

In another respect, however, the results reached seem to me to be interesting. We have been able to state during the cleavage a progressive torsion of the vegetative cells with regard to the animal cells which becomes especially manifest from a comparison of figs. 2, 4, 7, 9, 10, 12, and 14 and of figs. 3, 5, 6, 8, 11, 13, and 15. So we have every reason to assume that in the adult form also a similar arrangement of the cells prevails. In the spiral cleavage type the succeeding dexiotropic and laeotropic divisions nearly annul the effect of each other, so that in the blastula the cells belonging to one quadrant nearly occupy an area situated between two meridians distant 90° from each other, as is represented fig. 16*a*. Fig. 16*b* shows the situation of the cells belonging to one quadrant in the case where the torsion does not surpass 90°. How great the latter has become in the adult *Volvox* cannot be made out. Now in the same dexiotropic direction also the rotation occurs, as we have seen, and it seems to me probable that in this case we may look for a more direct relation between the two phenomena than with the torsion of Gasteropods. Let us assume to this end that not only the colony but also each of the cells of *Volvox* has a certain polarity and thus a main axis in the direction from the animal to the vegetative pole of the colony. This polarity of the cells e.g. manifests itself in the corresponding direction in which all the flagella beat causing a water current from in front backwards, which makes the organism move

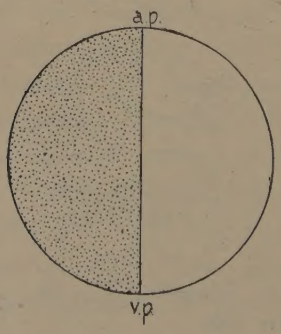

Fig. 16*a*.

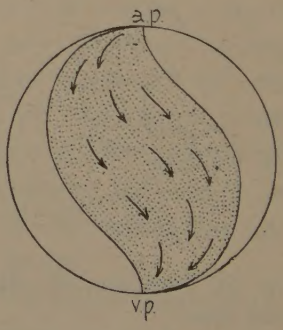

Fig. 16*b*.

in the direction of the animal pole. If a *Volvox* be pressed between a cover-slip and an object-slide so that it cannot move anymore, this

water current can easily be demonstrated by watching the little particles suspended in the water. If further we assume that by the dexiotropic torsion during the cleavage the direction of the main axis of the cells undergoes a dexiotropic deviation and the flagella thus beat in the direction of the arrows in fig. 16*b*, then the dexiotropic rotation of the colony follows directly from this assumption. That indeed the flagella beat in this way needs no further proof, but follows from the rotation itself.

It would be interesting no doubt if a variety of *Volvox globator* rotating to the left, were discovered. It can hardly be expected otherwise than that the cleavage here will equally belong to the inverse type.

Have we accounted now for the rotating movement of *Volvox* by the torsion presenting itself during the cleavage? In a causal sense we have, if our suggestion is right. But how is the torsion of the cleavage cells to be accounted for? Phylogenetically now I should feel inclined to consider the torsion during the cleavage rather as a consequence of the rotation of the adult animal than as its cause. The study of ontogeny ever anew teaches us that we must not consider the structure of the adult animal phylogenetically as a product of the developmental processes, but we rather must account for the latter by the structure of the adult animal. Thus I would see also in the torsion during the egg cleavage of *Volvox* nothing but a very precociously appearing character of the adult form related to the movement of the latter. This character, which cannot be demonstrated in the adult form, could be revealed only by the study of its development.